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METATHETIC REACTIONS BETWEEN CERTAIN SALTS IN SOLUTION IN LIQUID AMMONIA.

BY E. C. FRANKLIN AND C. A. KRAUS.

The great power of anhydrous ammonia as an electrolytic solvent, occupying as it does, of all known solvents, a position nearest to water in its power of dissociation[1] and in its capacity as a general solvent,[2] has led the authors to inquire whether or not metathetic reactions, similar to those which take place in aqueous solutions, do not take place also in ammonia solutions. If salts in solution in ammonia are dissociated to an extent approximating the dissociation in water solutions, then salts insoluble in ammonia should be precipitated rapidly and completely when ammonia solutions of salts containing the ions necessary for the formation of such substances are brought together. That in a considerable number of cases such action takes place, is shown by the experiments described in this paper.

Method of Making the Tests.

The nitrates of 16 metals, selected because of their ready solubility, together with the fact that they were at hand, were chosen to furnish the metallic ions, while the sulphide, chloride, bromide, iodide, chromate, and borate of ammonium constitute the list of salts which were used as precipitants.

[1] Cady: Jour. Phys. Chem., 1, 707 (1897). [2] This JOURNAL, 20, 820.

The tests were made by bringing together in a small vacuum-jacketed test-tube solutions of the nitrate and of the precipitant, and observing whether or not a precipitate was formed.

General Results.

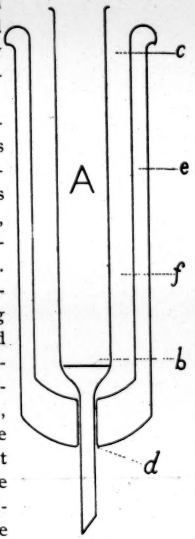
Ammonium Chloride as Precipitant (Table I).—Most of the metals tested are precipitated as chlorides by the action of ammonium chloride. Those chlorides, which by direct experiment were found to be entirely insoluble, separate immediately and completely when the two solutions are brought together, while those which were found to be slightly, or but moderately soluble, separate slowly and incompletely from more concentrated solutions.

Ammonium Bromide as Precipitant.—Table II gives the results obtained by the use of ammonium bromide as precipitant. As was to be expected, considering the greater solubility of the bromides, these precipitates formed more slowly than the corresponding precipitates of chlorides.

Ammonium Iodide as Precipitant (Table III).—Corresponding with the much greater general solubility of the iodides, but two metals, barium and strontium, gave precipitates with ammonium iodide, and even these, as the crystalline nature of the precipitates indicates, are probably very slightly soluble.

Ammonium Sulphide as Precipitant (Table IV).—A solution of ammonium sulphide was prepared by passing washed and dried hydrogen sulphide into liquid ammonia. The gas dissolved, forming a clear, colorless solution. Ammonium sulphide was also prepared by the action of liquid anhydrous ammonia on liquid hydrogen sulphide. To the hydrogen sulphide at the temperature of the carbon dioxide and ether bath, liquid ammonia was added, with the result that immediately a mass of white solid ammonium sulphide was formed. Excess of ammonia dissolved the solid to a clear solution. On cooling the solution, saturated at the boiling temperature of ammonia, to the temperature of the carbon dioxide and ether bath, there was an abundant separation of crystals. A small quantity of these crystals, as well as a

larger quantity of the white solid, were filtered off, freed from ammonia, and transferred to a specimen tube. Although no analysis of the solid was made, there can be scarcely any doubt of its identity as ammonium sulphide.



All the metals tested, with the exception of the alkalies, gave precipitates with ammonium sulphide. Only a portion of these precipitates, however, as their most obvious property, their color, indicates, can be identical with the precipitates formed in aqueous solutions. Certainly the lead precipitate, after removing it from the solution and drying it at the laboratory temperature, is lead sulphide. The remaining black precipitates have not been studied. The precipitates formed from barium, strontium, calcium, and magnesium solutions are especially interesting for the reason that these metals in aqueous solution give no precipitates with ammonium sulphide. It is the expectation of the authors to collect and analyze these four precipitates, but up to the present, this has been accomplished in the case of but one of them, and this with not entirely satisfactory results.

Magnesium Ammonium Sulphide, $2MgS.(NH_4)_2S.xNH_3$.

Preparation.—To a Dewar test-tube containing a fairly strong solution of magnesium nitrate, an ammonia solution of ammonium sulphide was added as long as a precipitate continued to be formed. In order to separate the precipitate from the liquid, the contents of the tube were poured upon a filter, of which the following is a description. In the figure, *A* is the filtering-funnel proper, consisting simply of a thin-walled tube of the shape and size indicated, and provided with a platinum Witt filtering-plate *b*. The filtering-tube is

held in place by means of corks at *c* and *d*; *e* is a vacuum-jacketed tube. The space *f* is filled with ammonia to a convenient height.

The precipitate, after being transferred to the filter, was washed several times with fresh quantities of ammonia, the filtration being accelerated by closing the mouth of the tube by means of a cork. The pressure of the supernatant gas forces the wash-fluid through rapidly. After sufficient washing the tube was removed from the ammonia-bath, both ends were closed, one of them by means of a cork carrying a drying-tube filled with soda-lime, and the ammonia allowed to pass off at the ordinary temperature.

Properties of the Precipitate.—The compound was a finely crystalline, white solid, which gave off the odors of ammonia and hydrogen sulphide at the laboratory temperature. Freshly prepared, it is completely soluble in water. After standing for a short time, exposed to the air, it was no longer entirely soluble, a result due undoubtedly to the formation of magnesium hydroxide by the action of the moisture and oxygen of the air.

Analysis of the Precipitate.—Portions of the compound, prepared as described above, were transferred as rapidly as possible to small weighing-tubes. These were weighed and dropped into bottles containing fuming nitric acid. The sulphuric acid formed and the magnesium were determined according to the usual methods :

The following results were obtained :

	I.	II.	III.
Weight of substance,	0.1691	0.1906	0.2780
Magnesium pyrophosphate,	0.1171	0.1266	0.1793
Barium sulphate,	0.3166	0.3954	0.5828
Magnesium,	0.0231	0.0274	0.0387
Sulphur,	0.0435	0.0537	0.0794
Per cent. magnesium,	13.60	14.44	13.92
" " sulphur,	25.70	28.19	28.37

These determinations, made each on a different specimen of the substance, indicate in the material analyzed the presence of 2 atoms of magnesium to 3 atoms of sulphur with varying quantities of ammonia. The results obtained proba-

bly harmonize best with the assumption that the compound is a double sulphide of ammonium and magnesium, containing 2 molecules of magnesium sulphide and 1 molecule of ammonium sulphide, together with ammonia of crystallization, which, being gradually given off at temperatures above the dissociation-point of the compound, is a sufficient explanation of the variable composition as found by analysis.

The calculated percentage composition of $2MgS.(NH_4)_2S.9NH_3$ is, magnesium 14.41 per cent., sulphur 28.82 per cent., ammonia 56.16 per cent.; of $2MgS.(NH_4)_2S.10NH_3$ is, magnesium 13.71 per cent., sulphur 27.42 per cent., ammonia 58.28 per cent.

Ammonium Chromate as Precipitant (Table V).—Chromic acid, which presumably goes into solution as ammonium chromate, dissolves sparingly. Its solution gives precipitates with all the metals tested with the exception of lithium and sodium.

Ammonium Borate as Precipitant (Table VI).—Boracic acid, which in solution in ammonia presumably forms ammonium borate, is but sparingly soluble. Its solution gives precipitates with all the metals tested with the exception of lithium, sodium, and potassium.

TABLE I.

Ammonium Chloride as Precipitant.

Salt.	Remarks.
Lithium nitrate,	precipitate, from concentrated solution.
Sodium nitrate,	no precipitate.
Potassium nitrate,	precipitate, from concentrated solution.
Calcium nitrate,	precipitate, immediate.
Strontium nitrate,	" "
Barium nitrate,	" "
Magnesium nitrate,	" "
Zinc nitrate,	" "
Manganese nitrate,	" " white.
Cobalt nitrate,	" " "
Nickel nitrate,	" " light violet.
Cadmium nitrate,	" "
Mercuric nitrate,	no precipitate.
Lead nitrate,	precipitate, from concentrated solution.
Silver nitrate,	" " " "
Copper nitrate,	precipitate, from concentrated solution, blue.

TABLE II.

Ammonium Bromide as Precipitant.

Salt.	Remarks.
Lithium nitrate,	precipitate, from most concentrated solutions.
Sodium nitrate,	no precipitate.
Potassium nitrate,	" "
Calcium nitrate,	precipitate, immediate.
Strontium nitrate,	" "
Barium nitrate,	" "
Magnesium nitrate,	" not immediate.
Manganese nitrate,	" immediate.
Zinc nitrate,	" not immediate.
Cobalt nitrate,	" immediate, white.
Nickel nitrate,	" " light violet.
Cadmium nitrate,	" "
Mercuric nitrate,	no precipitate.
Lead nitrate,	precipitate, from concentrated solution.
Silver nitrate,	" " " "
Copper nitrate,	precipitate, from concentrated solution, blue.

TABLE III.

Ammonium Iodide as Precipitant.

Salt.	Remarks.
Lithium nitrate,	no precipitate.
Sodium nitrate,	" "
Potassium nitrate,	" "
Calcium nitrate,	" "
Strontium nitrate,	precipitate, crystalline.
Barium nitrate,	" "
Magnesium nitrate,	no precipitate.
Zinc nitrate,	" "
Manganese nitrate,	precipitate, slowly.
Cobalt nitrate,	no precipitate.
Nickel nitrate,	" "
Cadmium nitrate,	precipitate, slowly.
Mercuric nitrate,	no precipitate.
Lead nitrate,	" "
Silver nitrate,	" "
Copper nitrate,	" "

TABLE IV.

Ammonium Sulphide as Precipitant.

Salt.	Remarks.
Lithium nitrate,	no precipitate.
Sodium nitrate,	" "
Potassium nitrate,	" "
Calcium nitrate,	precipitate, not immediate, white.
Strontium nitrate,	" immediate, white.
Barium nitrate,	" " "
Magnesium nitrate,	" not immediate, crystalline, white.
Zinc nitrate,	" immediate, white.
Manganese nitrate,	" immediate, white, dissolves on addition of water.
Cobalt nitrate,	" pinkish, on the addition of water the ppt. turns black.
Nickel nitrate,	" white, dissolves on addition of water.
Cadmium nitrate,	" white, on addition of water the precipitate becomes yellow.
Mercuric nitrate,	" immediate, black.
Lead nitrate,	" " "
Silver nitrate,	" " "
Cupric nitrate,	" yellowish brown, from concentrated solutions.
Bismuth nitrate,	" immediate, black.

TABLE V.

Ammonium Chromate as Precipitant.

Salt.	Remarks.
Lithium nitrate,	no precipitate.
Sodium nitrate,	" "
Potassium nitrate,	precipitate, slight, flocculent.
Calcium nitrate,	" flocculent.
Strontium nitrate,	" "
Barium nitrate,	" "
Magnesium nitrate,	" "
Zinc nitrate,	" "
Manganese nitrate,	" "
Cobalt nitrate,	" "
Nickel nitrate,	" "
Cadmium nitrate,	" "
Mercuric nitrate,	" "
Lead nitrate,	" "
Silver nitrate,	" "
Copper nitrate,	" "

TABLE VI.

Ammonium Borate as Precipitant.

Salt.	Remarks.
Lithium nitrate,	no precipitate.
Sodium nitrate,	" "
Potassium nitrate,	" "
Calcium nitrate,	precipitate.
Strontium nitrate,	"
Barium nitrate,	"
Magnesium nitrate,	"
Zinc nitrate,	"
Manganese nitrate,	"
Cobalt nitrate,	"
Nickel nitrate,	"
Cadmium nitrate,	"
Mercuric nitrate,	"
Lead nitrate,	"
Silver nitrate,	"
Copper nitrate,	"

UNIVERSITY OF KANSAS, June, 1898.

SOME PROPERTIES OF LIQUID AMMONIA.

BY E. C. FRANKLIN AND C. A. KRAUS.

The authors have been led to undertake the study of the properties of liquid ammonia in considerable detail with the object of following out, to as great an extent as possible, the manifest close relation which exists between this solvent and water. Although it has long been recognized that many derivatives of water have their analogues in certain ammonia derivatives, still the intimate relation existing between the two liquids seems never to have been fully recognized.

Water occupies an essentially unique position among the well-known solvents. Its physical properties, such as its capacity as a general solvent for salts and its power of electrolytic dissociation, its low molecular elevation constant, its high boiling-point, and its heat of fusion, heat of volatilization, critical temperature, and critical pressure, specific heat, association constant, and dielectric constant, with values so very much higher than the corresponding values for other

substances, all tend to remove it far from other solvents, and to place it in a class by itself.

From the considerations submitted below it will be recognized that, of all known liquids, ammonia most closely approaches water in all those properties which give to water its conspicuous position among solvents. In its capacity as a general solvent for salts it is secondary to water, but superior to all other solvents. It closely approaches water in its power of dissociating electrolytes; some salts conduct electricity even better in ammonia solution than they do in aqueous solution. It plays a part in many compounds analogous to that occupied by water in salts containing water of crystallization. Its heat of volatilization and probably its association constant are higher than those of any other liquid with the one exception of water. For a substance of such simple composition its critical temperature and critical pressure, and even its boiling-point at atmospheric pressure, are remarkably high, as is still more conspicuously true of the corresponding constants in the case of water. Its specific heat is quite as great as that of water, while its molecular elevation constant is lower than that of any other substance for which measurements have yet been made.

Ammonia differs from water in its inability to dissolve the sulphates and sulphites, the alkaline carbonates, phosphates, and oxalates, the hydroxides of the alkali and alkaline earth metals, and the facility with which it dissolves many organic substances, in which latter respect it reminds one of alcohol rather than of water. The liquid does not exhibit a maximum density[1] above the freezing-point nor is the solid ammonia specifically lighter than the liquid at its freezing-point, as is true of solid and liquid water.

Electrolytic Conductivity of Ammonia Solutions.—Bleekerode,[2] in a paper published in 1878, on the conductivities of the liquefied halogen acids, ammonia, and certain other compounds, makes the statement that liquid ammonia is a good conductor of electricity. There can be no question, however, that he misinterpreted his results. The conductivity he

[1] Faraday: Watts' Dict., 2d Ed., Vol. 1, p. 183.
[2] Phil. Mag. (5), **5**, 384 (1878), and Wied. Ann., **3**, 161, (1878).

measured was undoubtedly due to a salt of sodium in solution. The passage of the current decomposed the salt, setting free metallic sodium, which, dissolving in the ammonia, gave to the solution the characteristic blue color.

Divers, in 1873, observed that the concentrated solution of ammonium nitrate in liquid ammonia, formed by the deliquescence of the salt in an atmosphere of ammonia gas, is a good electrolytic conductor.[1]

Led to the subject by the study of the similarity of properties and of constitution of the compounds of salts with water of crystallization to those compounds in which ammonia plays an analogous part, Cady[2] discovered that solutions of certain salts in liquid ammonia are conductors of electricity. He measured the conductivity of 13 salts at moderate concentration, and found that they conduct electricity in ammonia solution at —38° almost, if not quite, as well as they do in water solution at 18°. He also found that solutions of the alkali metals conduct electricity, and with much greater facility than do salt solutions. Moreover he pointed out that these metallic solutions show no signs of polarization at the electrodes.

The authors have extended the list of determinations of the conductivity of metallic salts, and have also made measurements of the conductivity of certain organic compounds, especially the aromatic nitro-compounds, which show themselves to be good conductors in solution in ammonia. The authors have also made measurements of the increase of molecular conductivity with dilution for a number of salts, and have, further, determined the conductivity of a number of solutions at temperatures varying from —79° up to and past the critical temperature of ammonia. The results of this work will be published in the near future.

Metathetic Reactions in Ammonia Solutions.—As in the case of aqueous solutions, electrical conductivity and facility of chemical reaction between substances in solution go hand in hand, so, because of the undoubtedly dissociated condition of salts dissolved in liquid ammonia, precipitates ought to be

[1] Proc. Roy. Soc., **21**, 109 (1873). [2] Jour. Phys. Chem., **1**, 707 (1897).

formed instantaneously when solutions containing ions which are capable of forming salts insoluble in ammonia are brought together. That ammonia solutions do exhibit such behavior is shown by the results given in the preceding paper on "Metathetic Reactions between Certain Salts in Solution in Liquid Ammonia."

Ammonia of Crystallization and Ammonia of Constitution.—The authors have up to the present added but one compound to the long list of substances formed by the direct addition of ammonia to many of the metallic salts. Leaving out of consideration at the present time the very great number of such compounds, it will be sufficient to mention the early observations of Divers,[1] who considers the ammonia in the liquid formed by the action of ammonia on ammonium nitrate to be entirely analogous in function to the water absorbed, for instance, by calcium chloride; to the ammonia addition-products described by Joannis,[2] Jarry,[3] Bonnefoi,[4] formed by the action of liquid ammonia on the salts, and to the slaking phenomena attendant upon the action of liquid ammonia on certain halogen salts first described by Gore,[5] and also observed by the authors in their investigations on liquid ammonia as a solvent.[6]

Specific Heat of Ammonia.—The specific heat of liquid ammonia has been calculated from thermodynamic data by Zeuner, Ledoux, and Wood. It has also been made the subject of experimental investigation by Regnault, Von Strombeck,[7] Lüdeking and Starr,[8] and Elleau and Ennis.[9] For the experimentally determined values, Von Strombeck found 1.22876 at 45°, Lüdeking and Starr 0.8857 at 40°, and Elleau and Ennis 1.021 at 10°. Calculated from Professor Wood's formulæ[10] the values 0.98 to 1.14 at 10° are obtained.

Boiling-point of Ammonia.[11]—While the boiling-point of am-

1 *Loc. cit.* 2 Compt. rend., **112**, 337 (1891).
3 *Ibid.*, **124**, 288 and 963 (1897); **126**, 1138 (1898).
4 *Ibid.*, **124**, 771 (1897). 5 Proc. Roy. Soc., **20**, 441 (1872).
6 This JOURNAL, **20**, 820. 7 Jour. Frank. Inst., **130**, 467 (1890).
8 Am. J. Sci. (3), **45**, 200. (1893). 9 Jour. Frank. Inst., **145**, 189 (1898).
10 Thermodynamics, p. 325; Trans. A. I. M. E., **12**, 136, and **10**, 645.
11 Regnault gives 38°.5; Loir and Drion, 35°.7; and Bunsen, 33°.7 as the boiling-point of ammonia. Watts' Dict. Chem., 2d Ed., Vol. 1, p. 183; Supplement, Vol. 6, p. 102. Joannis gives the boiling-point at 38°.2, Compt. rend., **115**, 820 (1893).

monia is much below that of water, still it is high when compared with the boiling-points of other simple compounds of elements with low atomic weights. The boiling-points of hydrogen sulphide, hydrogen selenide, the halogen acids, methane, ethylene, acetylene, phosphine, and even arsine, stibine, and hydrogen telluride, are all below, and some of them far below the boiling-point of ammonia. As is the boiling-point of water, so is the boiling-point of ammonia, although to a less extent, abnormally high.

Heat of Fusion.—No determinations of the heat of fusion of solid ammonia have yet been made.

Heat of Volatilization of Ammonia.—With the exception of some preliminary measurements by the authors, no direct determinations of the heat of volatilization of ammonia at its boiling-point at atmospheric pressure have yet been made. Regnault's value[1] of 294.21 is the result of measurements made at 7°.8. Von Strombeck[2] obtained 292.4 as the result of measurements made at 14° to 18°. As preliminary results, the authors have obtained 326 to 332 as the heat of volatilization of ammonia at its boiling-point. A description of the method by which these measurements were made, together with the final values, will be published in a later paper.

The heat of volatilization of ammonia at any required temperature may also be calculated from thermodynamic formulæ. From a formula used by engineers in calculating the capacities of refrigerating-plants, $h_e = 300 - 0.8t$,[3] the value for the heat of volatilization of ammonia at —38° is calculated to be 330 calories.

Another formula given by Professor Wood,[4] $h_e = 555.5 - 0.613T - 0.000219T$, in which English heat units and Fahrenheit temperatures are to be understood, if used for calculating the heat of volatilization of ammonia, gives a value of 321 cal. at —38° C.

The heat of volatilization of a liquid may also be calculated by means of the law of Trouton,[5] according to which the molecular heats of volatilization of closely related substances

[1] Landolt und Börnstein, Physikalisch-chemische Tabellen.
[2] *Loc. cit.*, p. 472.
[3] Peabody : Thermodynamics, p. 459.
[4] Thermodynamics, p. 332.
[5] Phil. Mag. (5), 18, 54 (1888).

are directly proportional to their absolute boiling-points. In the expression for Trouton's law $\lambda M/T = k$, in which λ is the heat of volatilization, M the molecular weight, and T the absolute boiling-point, the values of k, in the case of water, methyl alcohol, ethyl alcohol, and amyl alcohol are respectively 25.9, 25.7, 26.3, and 26.2. If we are justified in assuming that ammonia is closely related to water, then by substituting the values, $k = 25.9$, $T = 235$, and $M = 17$, in the formula $\lambda = kT/M$, the latent heat of volatilization of ammonia is calculated to be 358 calories.

These values, while not in as good accord as might be wished, still agree in showing that the heat of volatilization of liquid ammonia, of all known liquids, is second only to water.

Molecular Elevation Constant of Ammonia.—Other than by direct experimental determination, the molecular elevation constant of a liquid may be calculated by means of the formula of Van't Hoff, provided the heat of volatilization and the boiling-point of the liquid are known. Several approximate values for the heat of volatilization of ammonia are given above, which by substitution in the formula, $k = 0.02T^2/\lambda$, yield the values given below for the molecular elevation. Values for the molecular elevation of the boiling-point, experimentally determined for a number of substances,[1] are also included in the table.

	k_e.	k.
Peabody's formula,	329	3.35
Wood's "	321	3.44
Trouton's "	358	3.09
H_e direct,	329	3.36
Water,		3.4
Ethyl alcohol,		3.4
Propyl "		3.4 to 2.7
Pyridine,		3.3 to 1.8
Aniline,		3.9 to 3.1
Potassium iodide,		3.2 to 5.9

Certainly the molecular elevation of the boiling-point of ammonia is smaller than that of any other solvent for which measurements have yet been made.

[1] This JOURNAL, **20**, 836.

The Dielectric Constant of Ammonia.—This constant has recently been measured by Dr. H. M. Goodwin,[1] of the Massachusetts Institute of Technology, who finds a value of about 20. These measurements, if Nernst's hypothesis holds true, show that the dissociation of salts in liquid ammonia may not be as great as we had supposed.

Molecular Association of Ammonia.—Some indication of the degree of association of a liquid may be arrived at by the application of the methods given by J. Traube in a recent paper.[2]

For liquid ammonia we have calculated the values, 190_{-38}, 23.9 and 0.00079, for x_2, $\frac{M\lambda}{T}$ and $\frac{M\,T' - T}{m\ \ pT}$, respectively,[3] results which place liquid ammonia among the associated liquids along with water and the alcohols.

If 55.90, the approximate molecular heat of volatilization of ammonia, be substituted in place of an incorrect value used in a table recently published by Vaubel,[4] then the association constant of liquid ammonia approaches that of water and excels that of the alcohols instead of indicating ammonia to be a non-associated liquid.

UNIVERSITY OF KANSAS,
September, 1898.

Contributions from the Laboratory of General Chemistry, University of Michigan.

ON THE CONSTITUTION OF THE PHENYLHYDRAZONES.

BY PAUL C. FREER.

Two possible constitutions can be assigned to the compounds of phenylhydrazine with ketones and aldehydes—the *hydrazone* or the *hydrazo* structure :

$$\begin{array}{l} RR'HC \\ \quad | \\ R''_2C.C : N.NHC_6H_5 \end{array} \qquad \text{or} \qquad \begin{array}{l} RR'C \\ \quad \| \\ R''_2.C.NH.NH.C_6H_5 \end{array}.$$

Attention has been called by others[5] to the fact that certain

[1] Paper read before Sec. B, American Association for the Advancement of Science, 1898.

[2] Ber. d. chem. Ges., **30**, 265 (1897).

[3] *Loc. cit.*, p. 273.

[4] Jour. prakt. Chem. (5), **57**, 351 (1898).

[5] V. Meyer und Jacobson: Lehrbuch II, 326; Nef: Ann. Chem. (Liebig), **270**, 289; **300**, 319; **280**, 294.

ketones react with phenylhydrazine by addition, first producing the hydrazone hydrates :

$$>CO + H_2N.NH.C_6H_5 = >C\begin{matrix}OH \\ NH.NH.C_6H_5\end{matrix};$$

but all such bodies have heretofore been either the anilides or methyl amides of ketone acids, *i. e.*, the anilides of mesoxalic, pyruvic, and benzoylpyruvic acids, and the methylamide of benzoylpyruvic acid. No other ketones have as yet given similar hydrates as, presumably, the compounds discovered by Wislicenus[1] are more of the nature of salts. I have noticed, however, that if the absolute ethereal solutions of aldehyde, methylethylketone, or similar aliphatic compounds, are cooled to —20°, and then mixed with absolutely pure, crystallized phenylhydrazine, a crystalline precipitate is at once formed, only to dissolve and disappear on standing for some time, while changing to the hydrazone. In all probability these precipitates consist of hydrazone hydrates, but whether this be true or not, I have no doubt that, in all cases in which hydrazones are formed, there is a previous addition of phenylhydrazine to the ketone or aldehyde, followed by a separation of water. This assumption is in entire accord with what we know in regard to the behavior of these bodies toward other reagents, such as ammonia or hydrocyanic acid, to use the most familiar examples. In these instances the hydrate happens, however, to be stable and consequently easily isolated. Once the addition of phenylhydrazine has taken place, it is obviously conceivable that the separation of water should take place in the one direction, in order to produce the hydrazone, or in the other, to form the hydrazo body, and, of course, it is also possible that representatives of both classes may be produced at the same time.

In considering the constitution of the phenylhydrazones, one fact is at once apparent : certain members of this class of bodies, such as the derivatives of acetone, methylethylketone, other aliphatic ketones, and acetophenone, are readily oxidized in the air, changing to non-crystallizable tars and at the

[1] Ber. d. chem. Ges., **34**, 2908.

same time giving off large quantities of gas, while others, such as pyruvic or acetoaceticether phenylhydrazones, are perfectly stable or at least change to other bodies which are *not* oxidation-products.[1] In a former article I called attention to this behavior[2] and suggested then that possibly this difference in behavior might be due to a difference in constitution. It is certain that this contrast would, in the past, have become a subject of investigation if it had been possible to isolate the products produced by oxidizing the former class of bodies but, in all probability, the attempts proved failures because of the difficulty of obtaining pure, crystallized substances; for I have discovered that these oxidation-products, when isolated, are extremely unstable. According to our present views it is generally accepted as true that the hydrazo structure R.NH.NH.R′ must be assigned to compounds which are converted into azo bodies by oxidation, especially if the former can readily be reproduced from the latter by reduction. In the course of this work I have found that acetone-*p*-bromphenylhydrazone, when carefully subjected to the action of air, is quantitatively changed to a red, explosive azo body, and that sodium amalgam as readily reverses the process, leaving the original substance as a final product. The same change can be accomplished in the same way with acetophenone-*p*-bromphenylhydrazone and with acetophenonephenylhydrazone, although in the case of the last body mentioned, the product is not crystallizable. Reduction accomplishes the same end with these compounds as it does with the acetone derivative. All of these azo bodies, in conformity with the behavior of azobenzene itself, form crystalline perbromides, which can also be reduced to the original hydrazones. The perbromides have such a characteristic appearance and undergo such typical changes on heating or on boiling with alcohol, that their formation can properly be used to identify the azo bodies themselves. Judging by these reactions, the above-mentioned hydrazones have the following general structural formula :

[1] Acetoaceticether phenylhydrazone changing to 1-phenyl-3-methyl-5-pyrazolone.
[2] Ann. Chem. (Liebig), **283**, 391.

$$\begin{array}{l} CH_2 \\ \| \\ C\text{—}NH.NHC_6H_4Br, \\ | \\ R \end{array}$$

because the corresponding azo bodies have the following constitution:

$$\begin{array}{l} CH_2 \\ \| \\ C.N : N.C_6H_4Br \\ | \\ CH_3 \end{array} \qquad \text{and} \qquad \begin{array}{l} CH_2 \\ \| \\ C.N : N.C_6H_4Br. \\ | \\ C_6H_5 \end{array}$$

In order to secure further proof that I really had to deal with substances containing the azo grouping, I investigated the oxidation of benzoyl-*p*-bromphenylhydrazine for purposes of comparison. Fischer[1] had already undertaken similar work with benzoylphenylhydrazine, obtaining, however, only an oil on oxidizing with yellow oxide of mercury. He was unable to crystallize or purify the body, but reconverted it into the mother-substance by reduction. I secured better results with the *p*-brominated compound, for the latter, when treated with the above-mentioned reagent, is readily changed into a fine, red, crystalline body which resembles those obtained from the hydrazones in every particular except that it is more stable; bromine converts the red crystals into a garnet-colored perbromide, which decomposes on boiling with alcohol, into nitrogen, benzoic ether, and brominated phenols in a manner exactly analogous to the behavior of the perbromides obtained from the oxidation-products of the hydrazones.

As there seems to be no doubt that many phenylhydrazones are readily oxidized to azo bodies, the question at once arises whether this reaction can be looked upon as absolute proof of the hydrazo structure of the original substances, and the answer is to be obtained by determining whether other changes which they can undergo, conform equally well with this view. As a result of this consideration I undertook the investigation of the action of benzoyl chloride on the substances in question. If

[1] Ann. Chem. (Liebig), **190**, 126.

acetonephenylhydrazone is dissolved in cold toluene and then mixed with benzoyl chloride, a slow reaction sets in and an insoluble syrup, in addition to the hydrochloride of the base, is produced. This syrup is readily converted into acetone and dibenzoylphenylhydrazine when treated with a dilute alcoholic solution of hydrochloric acid, so that a body which contains two benzoyl groups to each molecule has been formed, because dibenzoylphenylhydrazine but not a trace of the monobenzoyl compound is separated from it. Acetophenonephenylhydrazone behaves in the same way, dibenzoylphenylhydrazine, but none of the mono compound, being produced.[1]

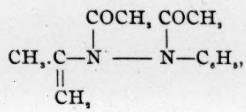
In contrast to the above, the phenylhydrazones of pyruvic ester and of benzophenone, both of them non-oxidizable and unquestionably true hydrazones, are not acted on by benzoyl chloride even when heated to 140°; indeed, the temperature reaches 165°–180° before a change sets in, and then there results a mixture of mono- and dibenzoylphenylhydrazine. So far, then, there seems to be a marked contrast between those bodies which can be oxidized to substances with azo structure and those which cannot. Overton[2] mentions a case in which acetyl chloride acts upon anisylphenylketonephenylhydrazone and describes what must be considered as an addition-product. This substance is a horn-like mass which absorbs moisture from the air, decomposing with water to form anisylphenylketone and monoacetylphenylhydrazine, again demonstrating a difference between the behavior of a true hydrazone and one of the class of bodies under consideration. In only very few instances have crystalline acyl substitution-products been obtained from phenylhydrazine derivatives of ketones and of the small number of bodies which have been so classed, one, at least, has proved to be of an entirely different structure.

Nef[3] studied the action of acetyl chloride on the hydrazone of acetoacetic ester and obtained what he considered to be a body of the following structure:

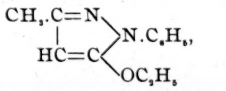
[1] β-Benzoïnphenylhydrazone also reacts with benzoyl chloride but in an entirely different manner. This will be discussed further on.

[2] Ber. d. chem. Ges., **26**, 23.

[3] Ann. Chem. (Liebig), **266**, 75.



and looked upon its formation as a further proof of the hydrazo formula of that substance. In the course of my work, however, it was demonstrated that the result of this reaction has the composition represented by $C_{15}H_{14}N_2O$,[1] and Walker[2] rendered the following constitution probable:



so that this presumed diacetyl substitution-product can no longer be classed as such. The only definitely described bodies of this class are therefore the pentabenzoyl derivative of phloroglucinphenylhydrazone,[3] the monoacetyl pyruvic aldehydrazone of Japp and Klingemann,[4] obtained by the action of acetic anhydride on pyruvic aldehydrazone and a tetrabenzoyl body derived from succinylosuccinicester phenylhydrazone which is very briefly mentioned by Nef.[5] In the first case, Von Baeyer and Kochendorfer have shown that the phenylhydrazone of phloroglucin is unquestionably a hydrazo body, for they oxidized it to the corresponding azo derivative, just as is the case with the bodies described by me; pyruvic aldehydrazone, on the other hand, has a different structure, and yields a monoacetyl derivative. So far as our experience reaches, therefore, it is evident that those hydrazones which can be changed to azo bodies react with benzoyl chloride, either to give non-crystallizable bodies from which dibenzoylphenylhydrazine can be obtained or they give, as is shown in one instance, stable derivatives in which acyl groups are substituted for both hydrazo hydrogen atoms. The true hydrazones, on the other hand, which, of course, cannot be oxidized to bodies with the azo structure, are either not acted on

[1] This JOURNAL, **14**, 487.
[2] *Ibid.*, **15**, 584.
[3] Ber. d. chem. Ges., **22**, 2192.
[4] Ann. Chem. (Liebig), **247**, 196.
[5] *Ibid.*, **266**, 76.

at all by acyl chlorides or they are converted into monoacylated derivatives, or into monosubstituted phenylhydrazines. These considerations furnish a further proof of the hydrazo nature of acetonephenylhydrazone and of acetophenonephenylhydrazone.

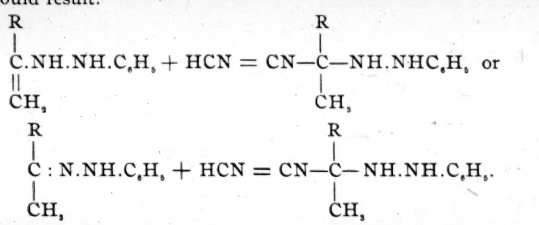
The majority of phenylhydrazones cannot be benzoylated according to the Baumann-Schotten method. Acetone-*p*-bromphenylhydrazone, acetophenone-*p*-bromphenylhydrazone, pyruvic phenylhydrazone did not react; acetoaceticester phenylhydrazone was saponified, yielding phenylmethylpyrazolone and non-crystallizable tars. It seems to be generally believed that phenylhydrazones should all react readily with acyl chlorides in such a way that the hydrogen atoms attached to nitrogen can be substituted. From what has gone before, however, it is evident that this is the case only in certain instances.

It would seem probable that these phenylhydrazine derivatives of aldehydes or ketones which can be readily converted into azo bodies should also react with benzoic aldehyde to form hydrazoïnes, just as hydrazobenzene itself does.[1] This is not the case, however, at least with acetonephenylhydrazone, for the latter body is quantitatively converted into benzalphenylhydrazine and acetone, even in the cold. Phthalic anhydride, on gentle heating, acts in the same way, phthalylphenylhydrazone being produced, but these negative results show how readily this phenylhydrazone is decomposed, a fact which again points to its hydrazo structure.

An unbiased opinion as to the structure of the bodies under discussion cannot be formed, however, unless the addition-reactions of Miller and Plöchl[2] with Schiff's bases and the phenylhydrazones of aldehydes and ketones are considered. These investigators demonstrated that hydrocyanic acid readily adds itself to the phenylhydrazones derived from aliphatic ketones or aldehydes, but that it is indifferent toward those of the aromatic or semiaromatic series. Pyruvic hydrazone forms an exception to the rule. Now it is apparent that

[1] Cornelius and Homolka : Ber. d. chem. Ges., **19**, 2239.
[2] *Ibid.*, **25**, 2020 ; **27**, 1281.

such additions could take place regardless of whether the unsaturated linking is between two carbon atoms or between a carbon and a nitrogen atom, for in either case the same product would result.[1]



It has been shown, so far as the investigation has been extended, that all aliphatic hydrazones (also acetone-*p*-bromphenylhydrazone, which yields an azo body) take up hydrocyanic acid with the exception of pyruvic acid phenylhydrazone, and the latter body, as will be shown below, does not possess the hydrazo structure. The conclusion might be drawn from these facts that pyruvic phenylhydrazone does not possess the same constitution as the others, but then we find that acetophenonephenylhydrazone—which undoubtedly yields an azo body—is also incapable of adding hydrocyanic acid, so that we are forced to the conclusion that Miller and Plöchl's reactions can prove neither the one nor the other constitution.

The present condition of our views as to structural chemistry, therefore, forces us to the belief that those hydrazones which can be readily oxidized to azo bodies, and react with benzoyl chloride in the manner outlined above, really have the hydrazo structure, for the oxidation of a body of the formula, , to an individual containing azo nitrogen although conceivable, is scarcely probable.

In view of the above considerations we should, however, be

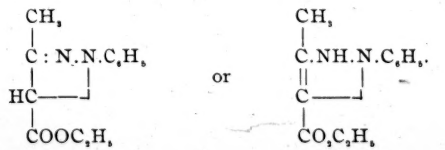
[1] Bredt and Kallen (Ann. Chem. (Liebig), **293**, 238) have demonstrated that hydrocyanic acid can add itself to the unsaturated linking of a pair of carbon atoms.

able to obtain substances belonging to both classes from the interaction between one and the same ketone or aldehyde and phenylhydrazine. This seems to be the case with the benzoïnphenylhydrazones. Smith and Ransom[1] have proved the existence of two benzoïnphenylhydrazones, one melting at 106° and the other at 159°, and naturally looked upon the same as geometric isomers. On applying the methods used in this investigation, however, it could readily be shown that these bodies are fundamentally different in their chemical behavior. When the low-melting substance is treated with benzoyl chloride in ethereal solution it undergoes a remarkable change into a new body, entirely different from either the α- or β-phenylhydrazones, but it nevertheless has the same composition and molecular weight, and consequently is an isomer. There are, therefore, in reality three benzoïnphenylhydrazones. β-Benzoïnphenylhydrazone, dissolved in ether and saturated with gaseous nitrogen trioxide, yields a garnet-colored, azo-like body which, however, is in reality an addition-product of the oxide and the presumed azo derivative. This addition-product gives a perbromide, just as the previously described simple substances do, the crystals of which have the same appearance and decompose in the same way. α-Benzoïnphenylhydrazone is not attacked by benzoyl chloride in the cold, and with nitrogen trioxide it yields a white crystalline precipitate which gives a body melting at 212° on treatment with alkalies. The latter is probably the tetrazone.[2] The new isomer does not react with benzoyl chloride, and is changed but little, if at all, by nitrogen trioxide. It is not, therefore, difficult to select the hydrazo body from the three hydrazones of benzoïn—the substance which is easily changed by benzoyl chloride and is so readily attacked by the oxide of nitrogen is undoubtedly the one. It is not unlikely that similar relationships exist between the acetaldehydrazones of Fischer,[3] but the investigation in this instance is beset with greater difficulty, owing to the fact that one body is converted into the other with such readiness. Both the α- and β-hy-

[1] This JOURNAL, **16**, 108. [2] Pechmann : Ber. d. chem. Ges., **26**, 1045.
[3] Ber. d. chem. Ges., **29**, 793.

drazones behave alike toward nitrogen trioxide, yielding a white, crystalline, and extremely explosive product, probably the nitroso derivative. If the latter is shaken with alkalies, it forms a yellow body, similar to that obtained from β-benzoïnphenylhydrazone, and this also forms a perbromide. β-Acetaldehydrazone is readily oxidized by yellow oxide of mercury, but the resulting substance, probably an azo body, is an oil, which, however, readily yields a perbromide; the α-phenylhydrazone is indifferent when treated with mercuric oxide. It does not seem likely, in view of the above, that the distinction between these two phenylhydrazones is one of geometric isomerism.

So far as I know, there is only one body directly derived by oxidizing an aliphatic phenylhydrazone, which is supposed to have the azo structure described in chemical literature. Nef[1] has shown that acetoaceticester phenylhydrazone can be oxidized by mercuric oxide to a red body, melting at 47°, which is generally considered to be benzeneazo-β-oxycrotonic ester, but it is also true that the same substance is produced by the action of phenylhydrazine on α-chloracetoacetic ester.[2] If we take the first formation alone into consideration, the azo structure would scarcely be open to question but, unless we accept the view that an atomic rearrangement takes place, it is impossible to obtain an azo body according to the second method; indeed, according to that synthesis one of the two following structural formulæ must result:



An investigation into the chemical behavior of benzeneazo-β-oxycrotonic ester increases the doubt as to its azo structure and renders the other formulæ more probable. The body does not give a perbromide, as is the case with analogous substances, but, on the other hand, bromine seems to cause

[1] Ann. Chem. (Liebig), **266**, 74. [2] Beuder: Ber. d. chem. Ges., **20**, 2747.

nearly complete decomposition into tarry products, from which but one pure body, described below, can be isolated. Reduction does not reproduce the mother-substance but, in place of the latter, phenylmethylpyrazolone and bisphenylmethylpyrazolone result. The substance in question melts quietly, without the evolution of a gas and, as Thiele[1] has demonstrated with the azo body obtained from hydrazoisobutyric acid and similar substances, and as is shown by the study of my semi-aromatic azo derivatives, all such bodies decompose and yield their nitrogen contents on being heated to a temperature slightly above their melting-points. Experiments with the object of obtaining substances similar to benzeneazo-β-oxycrotonic ester, by the method employed by Bender, have not succeeded in producing a parallel case. Hess[2] studied the action of bromacetophenone on phenylhydrazine and obtained a yellow, crystalline body. If this had the azo structure it would closely resemble the substance produced by me from acetophenone-*p*-bromphenylhydrazone, but investigation showed that its properties differed entirely from those of the latter, and that its molecular weight was greater than is represented by the formula $C_{14}H_{13}N_3$. Chloraldehyde hydrate simply yields a substance of the composition :

$$\begin{array}{l} CH_2\text{—}NH.NH.C_6H_5 \\ | \\ CH\text{=}N.NHC_6H_5 \end{array}$$

Chloracetone produces much more complicated bodies, neither do brom- or chlorlævulinic ester lead to the desired result.[3] The reaction with α-chloracetoacetic ester is, therefore, entirely different from those observed with the other α-halogen-substituted ketones, and, therefore, from lack of material for comparison, its azo structure cannot positively be denied ; nevertheless, its formation and its behavior point strongly toward the constitution given above, while, at the same time, the azo formula becomes doubtful.

[1] Ann. Chem. (Liebig), **290**, 33. [2] *Ibid.*, **232**, 234.
[3] Bender: Ber. d. chem. Ges., **21**, 2492.

EXPERIMENTAL DETAILS.

The Action of Benzoyl Chloride on Acetonephenylhydrazone.

10.9 grams of pure acetonephenylhydrazone were dissolved in 100 cc. of absolute ether, an excess of precipitated chalk added, and then the calculated quantity of benzoyl chloride poured in; the whole was then allowed to stand for one week at winter temperature, care being taken to shake frequently. At the expiration of this time the odor of benzoyl chloride was nearly gone, so that the precipitate was filtered, washed with water, and finally with dilute hydrochloric acid to remove the chalk, then dried and recrystallized from alcohol. It melted at 178°, and was dibenzoylphenylhydrazine. The filtrate, which had assumed a dark-red color, was evaporated *in vacuo*, leaving a dark oil, which gradually deposited a further quantity of dibenzoylphenylhydrazine. No other product could be isolated. In order, if possible, to separate the supposed addition-product, the reaction was repeated without the chalk, and with the substitution of toluene for ether as a solvent.

57 grams acetonephenylhydrazone were dissolved in 100 cc. toluene and then 15 grams ($\frac{1}{8}$ of the calculated quantity) of benzoyl chloride added, the whole being allowed to stand at ordinary temperature. At the expiration of twelve hours the solution had separated into two parts, an upper layer consisting of toluene, colored red, and a lower thick syrup, both sections being permeated with white crystals.

A. *The Crystalline Body.*—Recrystallized from acetone, this body separates in white plates with a luster resembling mother-of-pearl. It is soluble in water, and the addition of alkalies to the solution so produced precipitates an oil which does not reduce Fehling's solution. An analysis showed 19.15 per cent. chlorine to be present; calculated for the hydrochloride of acetonephenylhydrazone, 19.20 per cent. Acetonephenylhydrazone hydrochloride was prepared in ethereal solution by the action of hydrochloric acid gas and was shown to be identical with the substance under investigation.

B. *The Toluene Solution.*—This contained nothing but unchanged material and a trace of acetone.

C. *The Syrup.*—The syrup contains a large proportion of chlorine, and no method was found which could induce it to crystallize. It was consequently covered with pure ether, allowed to stand, the ether poured off, and this process repeated until all toluene, as well as any acetone which might possibly be present, was washed out. It was then covered with dilute pure alcohol to which a few drops of hydrochloric acid had been added, and allowed to stand. After a short time the whole nearly solidified to a crystalline mass of dibenzoylphenylhydrazine. A further portion of the syrup was covered with absolute alcohol and left over night, by which time some crystals of dibenzoylphenylhydrazine had separated. These were filtered and then 5 cc. of dilute hydrochloric acid were added to the filtrate, when a further separation of the same body took place. The latter was again separated, and then the brown mother-liquors were distilled, all that went over below 80° being collected. This portion was saturated with potassium carbonate, the supernatant fluid collected, fractionated, dried with fused sodium sulphate, and finally mixed with a concentrated solution of sodium bisulphite, whereupon the whole solidified to the characteristic flakes of acetone-sodium bisulphite. Pure acetone was then isolated from the latter in the usual manner. The syrup which is insoluble in toluene is, therefore, most probably a dibenzoyl compound of acetonephenylhydrazone, which is decomposed into acetone and dibenzoylphenylhydrazine by means of alcoholic hydrochloric acid. No monobenzoylphenylhydrazine could be isolated. The mother-liquors invariably contain thick, non-crystallizable tar, in addition to the above. I was unable to obtain anything definite by employing a mixture of benzoyl chloride, sodium and phenylhydrazine, in the presence of absolute ether.

The Action of Benzoyl Chloride on Acetophenonephenylhydrazone.

This reaction takes the same course as that just described as taking place with the corresponding acetone compound. 6.3 grams of acetophenonephenylhydrazone were dissolved in benzene, and then 3.4 grams of benzoyl chloride added,

the whole being constantly stirred. The change is complete after forty-eight hours. The solvent was then evaporated in a vacuum, the remainder being a thick, black oil, permeated with a few crystals which proved to be the hydrochloride of acetophenonephenylhydrazone. The oil was covered with a solution of hydrochloric acid in dilute alcohol, and after a short time crystals of dibenzoylphenylhydrazine formed, the mother-liquors containing acetophenone.

Benzoic anhydride (5.4 grams) and acetophenonephenylhydrazone (5 grams) were sealed in a tube and heated for eight hours at 100°. A semi-solid mass remained. On cooling, this was extracted with ether, the solvent leaving white crystals of dibenzoylphenylhydrazine. The ethereal solution contained benzoic acid and acetophenone. Benzoic anhydride, therefore, behaves as does benzoyl chloride; it separates the hydrazone into dibenzoylphenylhydrazine and acetophenone, while, at the same time, it is itself converted into benzoic acid. Attempts to benzoylate acetone-*p*-bromphenylhydrazone and acetophenonephenylhydrazone in the presence of caustic soda, according to the method of Baumann and Schotten, were failures because the substances in question were not attacked.

The Action of Benzoic Aldehyde and of Phthalic Anhydride on Acetonephenylhydrazone.

Acetonephenylhydrazone (6 grams) and benzoic aldehyde (5.4 grams) were dissolved in alcohol, mixed, and allowed to stand over night. At the expiration of this time a large quantity of crystals had separated. These were filtered and recrystallized, and proved to be benzalphenylhydrazone.

Acetonephenylhydrazone (6 grams) was heated over a free flame with the calculated amount of phthalic anhydride, until reaction began. The whole was then set aside and warmed from time to time until the reaction was completed. There remained a transparent, semisolid mass, which solidified when rubbed under water. The product was finally crystallized from alcohol and, when pure, melted at 149°, which shows that it is phthalylphenylhydrazone.

These two reactions show the ease with which acetonephenylhydrazone is separated into its component parts, and such a behavior is to be expected of a hydrazo body having the structure $\begin{matrix} CH_3 \\ \| \\ C.NH.NHC_6H_5 \\ | \\ CH_3 \end{matrix}$, but would scarcely be predicted of a hydrazone. It is scarcely to be doubted, as was mentioned in the introduction, that the hydrazones are produced from the hydrates, owing to a separation of water from the latter bodies, and exactly the same change takes place when benzoic aldehyde acts upon acetonephenylhydrazone, the structure of the latter still permitting it to act much in the same manner as free phenylhydrazine. The first change is therefore the addition of benzaldehyde to form the hydrate, as follows:

$$RHN.NH.C_6H_5 + C_6H_5CHO = C_6H_5.\overset{H}{\underset{RN.NH.C_6H_5}{C}}—OH$$

In the next stage of the reaction isoacetone separates, instead of water, as is the case with the phenylhydrazone hydrates:

$$C_6H_5\overset{H}{\underset{RN.NH.C_6H_5}{C}}—OH = C_6H_5—\overset{H}{\underset{N.NH.C_6H_5}{C}} + ROH.$$

Finally, the isoacetone changes to ordinary acetone. The same series of reactions undoubtedly take place in the case of phthalic anhydride.

The Action of Bromine on Acetonephenylhydrazone:—Acetone-p-bromphenylhydrazone.

54 grams of pure, crystallized[1] acetonephenylhydrazone

[1] If pure acetone, in ethereal solution, is treated with pure, recrystallized phenylhydrazine and the ether then evaporated *in vacuo*, the phenylhydrazone separates in crystalline form. Recrystallized from ligroïn it melts at 31°–32°. See also Arnold: Ber. d.chem. Ges., **30**, 1015.

were dissolved in 300 cc. of absolute ether, cooled with snow and salt, and then 58.3 grams of bromine gradually dropped in, care being taken to stir vigorously during the entire operation, and to exclude the air by means of carbon dioxide. The color of the bromine disappeared as soon as the drops came in contact with the liquid, and at the same time a white, crystalline substance began to separate. This latter was the hydrobromide of acetone-*p*-bromphenylhydrazone. When all of the halogen had been added, the whole was allowed to stand an hour longer in the freezing-mixture, after which time the precipitate was filtered in an atmosphere of carbon dioxide. This precaution is necessary because the white crystals soon become violet in the air, finally changing to a sticky tar. The product was thoroughly washed with ether, dried in a current of the same gas, and then covered with an excess of dilute caustic potash, by which means it was changed to a somewhat yellow mass of sandy crystals. The latter are washed with water until they are entirely freed from alkali, pressed, and then dried on a porous plate in an atmosphere of carbon dioxide. They are finally purified by repeated recrystallization from ligroïn. They consist of white, shiny plates melting at 98°–99°.[1] Analysis showed 34.7 per cent. bromine; calculated 35.3 per cent. If the ethereal mother-liquors are allowed to stand in the cold, a further separation of the hydrobromide of acetone-*p*-bromphenylhydrazone takes place. The yield is almost quantitative, only the very last residues yielding a little tarry substance and having the odor of bromine substitution-products of acetone. Any doubt as to the identity of the body produced is dispelled by the following experiments:

4 grams of the pure crystals were boiled with hydrochloric acid in a vessel connected with an inverted condenser for one-half hour; the solution was then rendered alkaline and the white precipitate filtered, dried, and weighed, the quantity being 3 grams (calculated 3.3 grams). The body produced crystallizes in long needles from hot water and has a melting-

[1] Absolutely pure acetone-*p*-bromphenylhydrazone melts at 98°–99° (uncorr.). The highest melting-point previously observed is that observed by Bamberger. This was 95° (Ber. d. chem. Ges., **30**, 217).

point of 105°–106°. Comparison with a preparation obtained in a different way, proved it to be *p*-bromphenylhydrazine. This method is the best, so far as I know, for preparing the latter substance.

A comparison of acetone-*p*-bromphenylhydrazone, formed by direct bromination, with a sample produced synthetically, also confirmed its identity.

This reaction is a general one with hydrazones, the only difference lying in the slight variation of detail necessary in each instance.

Acetophenone-p-bromphenylhydrazone.

24 grams of acetophenonephenylhydrazone were dissolved in 200 cc. of dry ether, cooled in a freezing-mixture, and 17.6 grams of bromine were gradually added, the liquid being meanwhile thoroughly stirred. A white, sticky mass begins to separate at once, and if a sample of this is spread on a porous plate it gradually changes to crystals which separate from hot water in needles melting at 106°, and are therefore *p*-bromphenylhydrazine. In order to avoid the formation of this body, the whole solution, including the precipitate, was thoroughly shaken with an excess of 10 per cent. caustic potash, as soon as all of the bromine had been added. It was then dried over fused sodium sulphate and the ether distilled off under diminished pressure. The remainder was a somewhat brownish, crystalline substance, which was purified by repeated crystallization from petroleum ether, the melting-point finally being 112°–113°. Analysis showed 27.73 per cent. bromine to be present; calculated 27.68 per cent. The yield was 25 grams of pure acetophenone-*p*-bromphenylhydrazone. A sample of the same body, prepared from acetophenone and *p*-bromphenylhydrazine proved its identity. The decomposition with hydrochloric acid is much slower and less satisfactory than it is in the case of acetone-*p*-bromphenylhydrazone.

If acetophenone-*p*-bromphenylhydrazone is slowly crystallized from alcohol, it separates in large cubes, resembling sodium chloride. It never shows a sharp melting-point for

the absolutely pure body begins to soften at 106°, and is only completely fluid at 113°. At a temperature somewhat above this it decomposes rapidly. Exposed to the air it is quickly oxidized, giving off a gas and changing to a black, tar-like substance. The fact that the body has not a sharp melting-point seemed to point to the existence of two isomers, but I have not, as yet, been able to prepare more than one acetophenone-*p*-bromphenylhydrazone.

The Action of Bromine on the Phenylhydrazone of Pyruvic Acid.

8.3 grams of the phenylhydrazone of pyruvic acid were suspended in ether and then 7.4 grams of bromine were added in the manner described above. The color of the bromine disappeared at once and the hydrazone went into solution. After the reaction was completed, the whole was extracted completely with 10 per cent. caustic potash, the alkaline extract acidified, the reddish precipitate dissolved in alcohol, and then separated by adding water. It was then a brown, amorphous powder. Its final purification is accomplished by dissolving it in potassium carbonate, boiling with animal charcoal, precipitating with dilute sulphuric acid, and finally recrystallizing from glacial acetic acid, when it appears as large yellow needles, melting at 184°. Analysis gave 31.1 per cent. bromine, calculated 31.4 per cent. The synthetical *p*-bromphenylhydrazone of pyruvic acid was identical with this body.

A chloroform solution of the phenylhydrazone of pyruvic acid ester is also easily brominated. The product melts at 132°, and is probably the *p*-brom compound.

Bromination of Ethylidenephenylhydrazone.

This reaction is essentially the same as that used in the formation of the acetone compound. The solid hydrobromide separates in ethereal solution, and the latter is shaken out with diluted caustic potash, the ether taking up all of the free body. After drying over fused sodium sulphate the solvent is evaporated *in vacuo* in the cold, by which means a crystalline product is obtained, separating from ligroïn in yellow

plates melting at 87°. This body is, therefore, ethylidene-*p*-bromphenylhydrazone.[1] If the product is slightly warm, as is the case if the ester is distilled in a water-bath, oxidation sets in so readily on exposure to the air, that a violent explosion may result. This was the case with one of the preparations which I made.

The phenylhydrazone of methylethylketone is attacked by bromine in the same way, the hydrobromide separating at first in the form of a white, crystalline precipitate. The latter is quickly covered with a dilute solution of sodium carbonate, care being taken to exclude air by means of a current of carbon dioxide. The product then separates as an oil, the ethereal solution of which, if it is evaporated rapidly *in vacuo*, deposits crystals, which, however, melt as soon as the temperature of the room is reached. The *p*-brominated body is oxidized very rapidly on exposure to the air. If the ethereal solution is allowed to stand for an hour, after the addition of bromine and before the liberation of the base by means of the alkaline carbonate, then only *p*-bromphenylhydrazine is obtained, so that there can be no doubt that the *p*-brominated phenylhydrazone is in reality formed. Methylethylketone-*p*-bromphenylhydrazone is therefore separated into its component parts with extreme ease.

Oxidation of Acetone-p-bromphenylhydrazone : p-Brombenzene-azo-i-propylene.

10 grams of pure acetone-*p*-bromphenylhydrazone were covered with 50 cc. of ligroïn (56°), placed in an Erlenmeyer flask, well stoppered, and allowed to stand at winter temperatures. The stopper was removed from time to time and the flask shaken vigorously for two or three minutes, and then again placed aside. The reaction was completed as soon as all of the crystals had dissolved and the liquid had assumed a deep orange color. The ligroïn was then drawn off by a current of dry carbon dioxide and, as its volume became less, large, orange-colored prisms, with red dichroism, began to form. The latter were purified by redissolving in the same medium and evaporating as before. The melting-point is 33°, above

[1] Neufeld : Ann. Chem. (Liebig), **248**, 95, gives the melting-point 83°.

which temperature the substance decomposes with explosive violence. When the prisms are exposed to the air, black spots soon begin to appear, and after a short time the entire substance breaks down with the evolution of nitrogen. Two grams of the body, ready for analysis and placed in a vacuum desiccator, exploded spontaneously with such violence that the apparatus was completely shattered and the fragments thrown to the corners of the room. The crystals cannot be kept for any great length of time, even in an atmosphere of carbon dioxide, although the decomposition under these circumstances is more gradual, and not violent. For this reason frequent recrystallizations are not possible. If the new body is gently warmed with concentrated sulphuric acid all the nitrogen is driven out. An analysis was therefore performed in the following manner: The substance was quickly weighed into a Kjeldahl flask, which had been previously filled with carbon dioxide; the apparatus was then connected with a Schiff azotometer, and a dropping-funnel containing concentrated, cooled sulphuric acid. After all air had been expelled the acid was rapidly added. Decomposition at once set in and was finally completed by gentle warming.

0.1880 gram substance gave 20.1 cc. nitrogen at 14°.5, and 737.8 mm.

	Calculated for $C_9H_9N_3Br$.	Found.
N	12.3	12.4

A molecular weight determination was carried out as rapidly as possible, the solvent used being benzene.

Benzene,	30.8759		
I. Substance,	0.1452	I. Depression,	0.11
II. "	0.5439	II. "	0.4

Calculated, 225; Found, I. 226; II, 232.

I was unable to obtain any accurate bromine determinations, as it was difficult to weigh and transfer the substance with sufficient rapidity; the numbers always appeared somewhat too low. The analyses of the perbromides, however, which are stable, were sufficiently accurate to make the analysis of the other compounds unnecessary.

The same body can be obtained in a much less pure condition by treating the hydrazone with yellow oxide of mercury in ethereal solution; the oxide is promptly reduced, and the liquid is at the same time colored red. After filtering and evaporating to dryness in a current of carbon dioxide, there remains an oil which gradually becomes semi-solid, and this has the properties of the body described above. It was found to be impossible successfully to recrystallize this product, as decomposition invariably set in before the desired object was accomplished. The change in acetone-*p*-bromphenylhydrazone is certainly due to oxygen, because a sample which was sealed in a small tube, from which the air had previously been expelled, suffered no alteration on standing for several months.

p-Brombenzeneazo-*i*-propylene is easily reduced to acetone-*p*-bromphenylhydrazone. 5 grams of the azo body were dissolved in absolute alcohol, sodium amalgam added, and one or two drops of hydrochloric acid, the contents of the flask being thoroughly shaken to hasten the change. The solution became colorless after a short time. When gas passed through freely, the supernatant liquid was decanted and diluted with water. Colorless, leafy crystals separated, which, when recrystallized from ligroïn, melted at 96°. This proved to be acetone-*p*-bromphenylhydrazone.

The Action of Bromine on p-Brombenzeneazo-i-propylene.

5 grams of the azo body were dissolved in cold chloroform, and then pure bromine gradually dropped in, the whole being kept cold. No change is observed during the first few seconds, but soon the bromine color disappears, and a yellow, crystalline body separates, there being no evolution of hydrobromic acid. The addition of bromine is continued until its color just becomes permanent. The precipitate is then filtered, dissolved in cold methyl alcohol, and the solution mixed with two or three times its own volume of ether; as a result yellow prisms gradually separate. The latter melt at 95°, with decomposition and separation of bromine. The same body can be prepared more readily by adding bromine to the

ligroin solution of *p*-brombenzeneazo-*i*-propylene, without taking the trouble previously to isolate the body. Bromine determinations gave the following results:

I. 0.0845 gram substance gave 0.1521 gram AgBr.

II. 0.0935 gram substance gave 0.1690 gram AgBr.

	Calculated for $C_9H_9N_2Br + 5Br$.	Found. I.	II.
Br	76.51	76.6	76.9

The perbromide is insoluble in ligroin. If it is warmed with water it gives off bromine. If boiled with benzene, bromine and a permanent gas separate. Repeated crystallization from luke-warm alcohol deprives the body of a portion of its bromine, giving a substance separating in yellow needles and melting at 102°–105°. This latter contains 73.63 per cent. bromine; calculated for $C_9H_9N_2Br + 4Br$, Br = 73.3 per cent. Continued boiling with alcohol finally causes complete decomposition of the perbromide.

It is possible to reduce the perbromide to acetone-*p*-bromphenylhydrazone. Two grams of substance melting at 95° were dissolved in alcohol, a drop or two of hydrochloric acid added, and then sodium amalgam poured in, the whole being vigorously shaken. As soon as the solution is colorless, it is poured off and diluted with water, when a crystalline body separates which is obtained from ligroin in flakes, melting at 93°–94°. This was consequently acetone-*p*-bromphenylhydrazone. Any doubt as to the nature of the products just described is finally removed by the following experiment: If acetone-*p*-bromphenylhydrazone (instead of the azo compound) is dissolved in chloroform, carefully cooled, and then bromine gradually added, hydrobromic acid is given off, and the same perbromide melting at 94°–95°, as was obtained from benzeneazo-*i*-propylene, and which in this latter instance is produced without the separation of hydrobromic acid, is separated on rubbing with a glass rod. Entirely different results are obtained, however, if the bromine is added carelessly, without the precaution being taken to cool thoroughly. The liquid then assumes a deep-violet color, nitrogen and hydrobromic acid separate rapidly, and the solution separates a certain

quantity of the hydrobromide of acetone-*p*-bromphenylhydrazone. If the latter is filtered and the mother-liquors (which now have the penetrating odor of halogen substitution-propucts of acetone) evaporated, there appear, in addition to a large quantity of tar, crystals which are free from nitrogen and melt at 87°. These have the appearance of *p*-dibrombenzene. In addition to the latter a small quantity of the hydrobromide of a body melting at 105° and probably *p*-bromphenylhydrazine, is obtained.

Oxidation of Acetophenone-phenylhydrazone by Yellow Oxide of Mercury.

10 grams of the hydrazone were dissolved in 25 cc. of ether, 1.5 gram-molecules of yellow oxide of mercury added, and the whole allowed to stand in a sealed tube, the latter being well shaken from time to time. The oxide is gradually reduced, the solution assumes a red color, and the reaction is complete after three to four days, no pressure being observed on opening the tube. The mercury and unchanged oxide are now filtered off, and the solution evaporated in a current of carbon dioxide. The remainder is a semi-solid mass which cannot be crystallized. It is rapidly oxidized when exposed to the air; heated on a platinum spatula it decomposes with a weak explosion; warmed with water or with sulphuric acid the substance gives off nitrogen; sodium amalgam reduces it, giving back acetophenonephenylhydrazone. There seems scarcely any doubt that this body is benzene-azo-*i*-styrene, but as yet it has not been obtained in a pure state. Better results are obtained with the *p*-brominated compound. If a sealed tube, filled as above, is allowed to stand too long, say for two or three weeks, there is then considerable pressure on opening, and none of the decomposable oil is obtained, obviously because the azo body has been completely broken down.

Oxidation of Acetophenone-p-bromphenylhydrazone : p-Brombenzene-azo-i-styrene.

10 grams of acetophenone-*p*-bromphenylhydrazone were covered with 50 cc. petroleum ether, the flask stoppered and

exposed to the temperature of winter. Care was taken to admit the air from time to time, just as was the case with the corresponding acetone derivative. Oxidation took place more slowly in this case but, after ten days, all had gone into solution, and at the same time the liquid had assumed a deep-red color. The petroleum ether was now cooled to —20°, and a separation of canary-colored prisms took place. The latter were filtered, once more dissolved, and again crystallized. They melted at 48°, and decomposed violently above that temperature. Exposed to the air they behaved as did benzeneazo-*i*-propylene, exploding after a certain time. The bromine was determined by the lime method, in a long tube, care being taken to weigh as quickly as possible.

0.1340 gram substance gave 0.0851 gram AgBr.

	Calculated for $C_{14}H_{11}N_2Br$.	Found.
Br	27.8	27.00

The substance decomposes, when gently warmed with sulphuric acid, nitrogen being evolved.

2 grams of the azo body were dissolved in alcohol, a drop or two of hydrochloric acid added, and then sodium amalgam poured in. As soon as the color of the solution disappeared, the supernatant liquid was poured off and diluted with water. The crystalline precipitate separated from alcohol as a body melting at 104°, and having all of the properties of acetophenone-*p*-bromphenylhydrazone.

If *p*-brombenzeneazo-*i*-styrene is dissolved in chloroform, well cooled, and bromine gradually added, a precipitate at once begins to appear, without evolution of hydrobromic acid. This substance crystallizes from alcohol, after ether has been added, in long prisms melting at 108°. In appearance and properties these are very closely like those obtained from the corresponding acetone derivative. The estimations of bromine gave results lying between the numbers required for $C_{14}H_{11}N_2Br + 7Br$ and those for $C_{14}H_{11}N_2Br + 6Br$. Found, bromine I. 74.1 per cent., II. 74.5 per cent. Calculated for $C_{14}H_{11}N_2Br + 7Br$; Br = 75.5; for $C_{14}H_{11}N_2Br + 6Br$, Br = 73.03. From these results it follows that this perbromide is a

mixture of the two bodies. Owing to its close resemblance to the perbromide of the corresponding acetone derivative, no further work was done with it at present.

It was not found possible to oxidize acetophenone-*p*-bromphenylhydrazone to an azo body by means of yellow oxide of mercury. The action takes place so slowly in the cold that the resulting compound is further decomposed. If the solution is warmed, the oxide is reduced rapidly, but on the other hand the azo body is at once completely broken down with the evolution of nitrogen.

In order to remove any doubt as to the nature of the bodies which have been described above, I have studied the behavior of benzoylphenylhydrazine. The work of Freer and Sherman[1] on formylphenylhydrazine has demonstrated that, in all probability, the acylphenylhydrazines have the structure $RO.NH.NH.C_6H_4$, so that they in reality constitute a series of hydrazo compounds.

The Action of Bromine on Benzoylphenylhydrazine: Benzoyl-p-bromphenylhydrazine.

Monobenzoylphenylhydrazine (20 grams) was suspended in 250 cc. of absolute ether, cooled in a freezing-mixture, and then 2 gram-molecules of bromine gradually added, the whole being well stirred. The bromine color disappeared at once, and a violent evolution of hydrobromic acid took place. After the action was complete, the resulting compound was filtered, washed with ether, and then quickly covered with dilute potassium hydroxide solution, by which means a white, crystalline body formed. The latter separated from alcohol in shiny, white leaflets, melting at 156°, with decomposition. The alcoholic mother-liquors, when diluted with water, deposit a smaller quantity of another body which fuses at 125°. This is probably the *m*-compound. It has not, as yet, been further investigated. Boiling hydrochloric acid splits the substance of melting-point 156° into benzoic acid and *p*-bromphenylhydrazine.

The first bromination of benzoylphenylhydrazine never is quite complete, for a certain quantity of unchanged body al-

[1] This JOURNAL, 18, 570.

ways remains. It is, therefore, advisable to carry out a bromine determination with the crude product, and then to repeat the above operation, using the calculated quantity of bromine. After subsequent recrystallization, the pure benzoyl-*p*-bromphenylhydrazine, melting at 156°, is obtained. Analysis resulted as follows:

0.4955 gram substance gave 0.2189 gram AgBr.

	Calculated for $C_{13}H_{11}N_2OBr$.	Found.
Br	27.41	27.42

Oxidation of Benzoyl-p-bromphenylhydrazine. p-Brombenzeneazobenzoyl.

Fischer[1] has already studied the oxidation of benzoylphenylhydrazine, but he obtained only a dark red oil, which he was able to reduce back to benzoylphenylhydrazine. The oil decomposed violently on heating and was completely broken down by boiling water. It undoubtedly, therefore, contained an azo body. Better results are obtained with the *p*-brom-compound.

10 grams of benzoyl-*p*-bromphenylhydrazine were suspended in 100 cc. absolute ether, 1.5 gram-molecules of yellow mercuric oxide added, and the whole set aside, the flask being well shaken from time to time. Reduction of the oxide takes place slowly, but after twelve hours the benzoyl-*p*-bromphenylhydrazine had dissolved and the liquid had assumed a red color. The solution was now filtered and the ether evaporated *in vacuo*, a red, crystalline body separating. This residue was extracted with cold ligroin, by which means the azo body was dissolved, and unchanged substance left behind. *p*-Brombenzeneazobenzoyl separated in red, leaf-like plates, when this solvent was evaporated in the cold. This operation was repeated several times, the body being finally dissolved in alcohol and recrystallized by adding water. Large red plates, melting at 69° and giving the following results on analysis, were obtained:

0.1877 gram substance gave 0.3696 gram CO_2, and 0.0533 gram H_2O.

[1] Ann. Chem. (Liebig), **190**, 126.

	Calculated for $C_{13}H_9N_2OBr$.	Found.
C	53.98	53.70
H	3.11	3.15

When pure, the azo body is perfectly stable in the air, heated in a tube it begins to give off nitrogen at 133°, and forms benzoic acid at 142°.

The reduction is easily accomplished. Two grams were dissolved in alcohol, sodium amalgam added, and the whole well shaken. As soon as the solution became colorless, it was decanted and acidified. The resulting precipitate, when recrystallized from alcohol, melted at 155°, and proved to be benzoyl-*p*-bromphenylhydrazine.

The Action of Bromine on p-Brombenzeneazobenzoyl.

The red crystals of the azo body were dissolved in chloroform and gradually mixed with a slight excess of bromine. Reaction set in, and only traces of hydrobromic acid were given off. At the same time a dark-red oil separated. This latter solidified completely on standing at a low temperature. The chloroform was then poured off and the crystals were spread on a porous plate. Two bodies were present, garnet-red prisms, melting at 123° with decomposition, and yellow needles, fusing at 106°. The red crystals rapidly lose bromine in the air and change to the yellow body. They were separated mechanically as soon as possible, and analyzed without further purification. Found, bromine 68.7 per cent.; calculated for $C_{13}H_9N_2OBr + 5Br$, $Br = 69.6$ per cent.[1]

If the red substance is covered with alcohol it at once changes to the yellow one. If the bromination is carried on as above, glacial acetic acid being substituted for chloroform, then the yellow body melting at 106° is alone produced. Analysis of the latter gave 65.7 per cent. bromine; calculated for $C_{13}H_9N_2OBr + 4Br$, $Br = 65.7$ per cent.

If either perbromide is boiled with alcohol, the latter is oxidized to aldehyde, nitrogen separates, and the solution be-

[1] These figures agree very nearly with those calculated for the perbromide of diazobenzene (calculated 69.56 per cent.), and it is possible that in some instances this body is formed. This question has not as yet been decided, but the whole subject of these perbromides and their decomposition will be thoroughly investigated next year.

comes colorless. When cooled, two bodies which are difficult to separate by fractional crystallization, appear; the one is in long needles, melting at 119°–120°, the other in prisms fusing at 87°. Neither contains nitrogen. Judging from the analysis and molecular weight, these bodies are bromine substitution-products of phenols, but as it has been demonstrated that this decomposition of perbromides of the class under study is a general one, and as it perhaps will lead to new methods of formation of bromine substitution-products of benzene no further work was done along this line.

The Action of Bromine on Monoacetylphenylhydrazine: Acetyl-p-bromphenylhydrazine.

This reaction was carried out exactly as with the corresponding benzoyl derivative. The resulting body at first is fluid, but solidifies after a time, especially if it is spread on a porous plate. Crystallized from alcohol with the addition of animal charcoal, it melted at 161°; the yield was unsatisfactory. When treated with mercuric oxide the body is changed to a red oil, which gives a yellow perbromide on treatment with bromine; this perbromide, when it is boiled with alcohol, decomposes in the same way as those described above.

The close resemblance between *p*-brombenzeneazobenzoyl, *p*-brombenzeneazo-*i*-propylene, and *p*-brombenzeneazo-*i*-styrene seems to remove all doubt as to the character of the latter two compounds.

In view of the above work it seemed desirable to discover whether acetone-*p*-bromphenylhydrazone, which is so easily oxidized to an azo body, would also take up hydrocyanic acid in the same way as the phenylhydrazones of Miller and Plöchl.[1] No action takes place if the hydrazone is diluted with absolute ether, but if it is covered with pure hydrocyanic acid and sealed in a tube, a gradual change takes place, the leaf-like crystals being converted into prisms. The reaction is completed in three weeks. The tube is then opened, the excess of hydrocyanic acid evaporated, and the product recrystallized from ligroin. It forms hard prisms which differ markedly from the original substance by being perfectly stable

[1] Ber. d. chem. Ges., **25**, 2058.

in the air; the melting-point is 95°–96°. A nitrogen determination gave the following results:

0.1116 gram substance gave 16.8 cc. nitrogen at 19° and 736 mm.

	Calculated for $C_{10}H_{13}N_3$.	Found.
N	16.5	16.8

This result proves that acetone-*p*-bromphenylhydrazone takes up hydrocyanic acid and if, as seems most probable from the above work, this body is in reality *p*-brombenzene-hydrazo-*i*-propylene, $\begin{matrix} CH_3 \\ \| \\ C \\ | \\ CH_3 \end{matrix}$—NH.NH.$C_6H_4$.Br, the addition must take place to the unsaturated pair of carbon atoms, the same must then be true of the other easily oxidized ketonephenylhydrazones which Miller and Plöchl investigated. From the researches of the latter it appears that the phenylhydrazone of pyruvic acid, which undoubtedly has the true hydrazone structure, does not take up hydrocyanic acid, but, on the other hand, acetophenone-phenylhydrazone, which can also be easily oxidized, is incapable of taking up hydrocyanic acid, so that, in the present state of our knowledge, we must conclude that this reaction can neither prove nor disprove the hydrazo structure.

Reactions with the Phenylhydrazone of Pyruvic Acid.

The phenylhydrazone of pyruvic acid is a body which shows an entirely different behavior from those which have been cited above, with the sole exception that it can be converted into the *p*-brom compound with equal ease. The substance is remarkably stable, does not oxidize in the least when exposed to the air, and is not changed to an azo body by mercuric oxide, neither does it form a tetrazone, as Von Pechmann found to be the case with benzalphenylhydrazone.

The Action of Mercuric Oxide on the Phenylhydrazone of Pyruvic Acid.

If the phenylhydrazone of pyruvic acid (15 grams), yel-

[1] Ber. d. chem. Ges., **26**, 1045.

low oxide of mercury (25 grams), and alcohol (100 cc.) are boiled in a vessel provided with an inverted condenser, the oxide is gradually reduced, and exactly one-half of the possible quantity of carbon dioxide separates (calculated CO_2, 12.6 per cent.; found, 12.9 per cent.); the evolution of gas then ceases and the reaction is complete. The mercury compound is then filtered off, and the alcohol evaporated *in vacuo* until crystals begin to appear. On standing, a yellow, crystalline powder separates. This is filtered off, extracted with 10 per cent. caustic potash in order to remove any possible unchanged substance, and at last recrystallized from alcohol with the addition of animal charcoal. The compound forms yellow needles, scarcely soluble in cold alcohol, easily taken up by the hot alcohol, separating from dilute acetic acid in large crystals melting at 186°.5.

0.1102 gram substance gave 0.0619 gram H_2O, and 0.2642 gram CO_2.

0.1522 gram substance gave 25.2 cc. nitrogen at 18° and 742.3 mm.

	Calculated for $C_{17}H_{18}N_4O_2$.	Found.
C	65.8	65.38
H	5.8	6.24
N	18.0	18.66

The molecular weight determination was made in a solution of glacial acetic acid.

Solvent, 22.08 Depression, 0.18
Substance, 0.3065

Calculated 310; found 308.

This body is therefore formed from the hydrazone of pyruvic acid according to the following equation:

$$2C_9H_{10}N_2O_3 + HgO = C_{17}H_{18}N_4O_2 + CO_2 + Hg + H_2O.$$

Reduction in acetic acid solution by means of zinc dust gave only aniline and tarry products. On adding alkali a large quantity of phenylisonitril was produced. Hydrochloric acid (33 per cent.) at 100°, chars the substance, splitting off one-half of the phenylhydrazine. No other body could be isolated.

Three grams of the substance were boiled with 2 gram-molecules of alcoholic potash for half an hour. On evaporating the alcohol and acidifying, a yellow body separated. This was filtered and recrystallized from acetic acid. It proved to be the phenylhydrazone of pyruvic acid. The mother-liquors were extracted with ether, the solvent evaporated, and the remainder recrystallized from benzene, when needles, melting at 126°, separated. Comparison showed these to be monoacetylphenylhydrazine. This oxidation product is therefore split into acetylphenylhydrazine and the phenylhydrazone of pyruvic acid by means of alkalies. It is therefore most probably the acetylphenylhydrazide of the phenylhydrazone of pyruvic acid, $CH_3.C : N.NH.C_6H_5$

$$\begin{array}{l} \\ | \\ OC.N.NH.C_6H_5. \\ | \\ COCH_3 \end{array}$$

The action of mercuric oxide on the hydrazone of pyruvic acid is therefore radically different from its action on the phenylhydrazones described above; the hydrogen present in the phenylhydrazine group is not attacked at all, but instead of this, carbon dioxide is eliminated, 2 molecules are joined, and the ethylidene group in one portion is oxidized to acetyl. This change would seem to prove that the phenylhydrazone of pyruvic acid has a constitution different from that of the class of bodies which can be oxidized to substances having the azo structure. It therefore is a true hydrazone, the others being hydrazo compounds. Other true hydrazones, such as benzaldehydrazone, as Von Pechmann demonstrated,[1] also behave differently from hydrazo compounds, for amyl nitrite or mercuric oxide changed this body into dibenzaldiphenyltetrazone. Many phenylhydrazones are not attacked at all by mercuric oxide. This is the case with the phenylhydrazone of pyruvic acid ester.

In view of the above results, it was necessary, if possible, to discover some case in which both classes of bodies are formed from one and the same ketone or aldehyde, as was mentioned in the introduction, all such attempts have as yet

[1] Ber. d. chem. Ges., **26**, 1045.

failed with acetone-*p*-bromphenylhydrazone and with acetophenone-*p*-bromphenylhydrazone. On the other hand, the desired substances seem to exist in the case of the benzoïnphenylhydrazones.

Reactions with the Phenylhydrazones of Benzoïn.

Smith and Ransom[1] have already demonstrated that an isomer of ordinary (159°) benzoïnphenylhydrazone can be obtained under certain circumstances. This isomer melts at 106° and, according to the usually accepted views, two bodies were considered to be stereoisomeric. That this is not the case, however, and that they are structurally different, is demonstrated by the facts stated below.

The Action of Benzoyl Chloride on β-Benzoïnphenylhydrazone: γ-Benzoïnphenylhydrazone.

Pure β-benzoïnphenylhydrazone, melting at 106°, is prepared by boiling a mixture of 20 grams of pure benzoïn and 10 grams of recrystallized phenylhydrazone in alcoholic solution in a vessel provided with an inverted condenser for three and a half hours. On cooling and standing in an ice chest over night, crystals separate which are filtered and purified from alcohol. On adding water to the mother-liquors, a mixture of the α- and β-compounds is obtained. Pure β-benzoïnphenylhydrazone must be perfectly soluble in cold glacial acetic acid.

5 grams of this body were dissolved in absolute ether and then an equal amount of pure benzoyl chloride added. After a few hours the solution became turbid and in the course of two days the reaction was completed. A mixture of shiny leaflets and an amorphous powder had now separated and the ether was colored red. The precipitate was repeatedly triturated with water, by which means the soluble, amorphous substance, which is the hydrochloride of a base, is separated, and the residue is finally recrystallized from alcohol. The pure substance weighed 2.7 grams. It forms plates with mother-of-pearl luster, melting at 162°.

I. 0.1879 gram substance gave 0.5452 gram CO_2, and 0.1040 gram H_2O.

[1] This JOURNAL, 16, 108.

II. 0.1667 gram substance gave 14 cc. nitrogen at 31° and 743 mm.

	Calculated for $C_{20}H_{18}N_2O$.	Found. I.	III.
C	79.43	79.13	....
H	5.96	6.09	....
N	9.27	....	9.42

The molecular weight determinations were carried out in a solution of methyl oxalate.

Methyl oxalate I.	27.483	Depression I.	0.08
" " II.	33.313	" II.	0.19
Substance I.	0.1281		
" II.	0.4168		

Calculated 302 ; Found, I. 298 ; II. 339.

These result show that this body is a third benzoïnphenylhydrazone. In appearance and solubility it differs entirely from the other two; the latter crystallize from alcohol in needles and are soluble in ether, the former separates from the same medium in plates, and is nearly insoluble in ether. I will designate this new compound as γ-benzoïnphenylhydrazone during the further discussion.

When the ethereal mother-liquors, obtained during the preparation of γ-benzoïnphenylhydrazone were evaporated, there remained a dark-red oil which had a strong odor of benzoyl chloride. On standing, a small quantity of the new body, and finally long, needle-like crystals separated from this. The benzoyl chloride was removed from the latter as far as possible, by adding petroleum ether and then pumping off the solution rapidly. On evaporation, 2.8 grams of unchanged benzoyl chloride remained. This separation is not strictly accurate, as a certain proportion of the chloride is always retained by the tarry mass surrounding the crystals, so that it must be assumed that the major portion remained unchanged during the reaction. A part is undoubtedly used up in forming the soluble hydrochloride above referred to, and some enters into the formation of the sticky decomposition-product. Further experiments with much less than the calculated quantity of benzoyl chloride demonstrated that such a large addition of that substance is by no means necessary to bring

about the change, so that benzoyl chloride does not directly enter into the composition of the bodies which are produced. The long, needle-like crystals were covered with a thick tar which was insoluble in petroleum ether. They were therefore spread on a porous plate and finally repeatedly recrystallized from alcohol, their total weight finally being 1.7 grams. This body contained no nitrogen, melted at 94°–95°, and comparison with other samples proved it to be benzil. The formation of this latter body is not due to absorption of oxygen from the air, for the same result is obtained if the reaction is allowed to go on in a flask filled with carbon dioxide. The total result was therefore as follows: From 5 grams of β-benzoïnphenylhydrazone and 5 grams of benzoyl chloride I obtained 2.7 grams of γ-phenylhydrazone, 1.7 grams of benzil, 3 grams of unchanged benzoyl chloride, and the remaining 2.6 grams consisted of the non-crystallizable tar and the small proportion of soluble hydrochloride. Benzoyl chloride therefore reacts with β-benzoïnphenylhydrazone in a most unexpected manner. The greater part is changed into the γ-phenylhydrazone, which undergoes no further change, and another portion forms benzil, and as a result of this secondary change, probably also the tarry products above referred to.[1] The origin of the benzil is not at all plain; it does not seem probable that it is produced by the oxidation and subsequent splitting down of the benzoïnphenylhydrazone, neither does it seem likely that it results from a union of two benzoyl groups derived from the chloride. A further detailed investigation of this point with larger quantities of material, is necessary.

Neither α- nor γ-benzoïnphenylhydrazone reacts with benzoyl chloride at ordinary temperatures.

There are some further points in connection with the preparation of α- and β-benzoïnphenylhydrazones which should be mentioned. Pickel[2] and Vogeltheer[3] obtained the α-compound only, their method consisting in boiling an alcoholic

[1] Smith and Ransom found that β-benzoïn-phenylhydrazone was completely decomposed by acetyl chloride. The formation of tarry products is always observed when benzoyl chloride acts on the hydrazones.

[2] Ann. Chem. (Liebig), **232**, 229. [3] Ber. d. chem. Ges., **25**, 637.

solution of benzoïn and phenylhydrazine for some time, then evaporating and extracting the syrup which remained with acetic acid, in order to remove phenylhydrazine. The reason why they obtained no β-phenylhydrazone was not because it was not formed, but because this substance is soluble in acetic acid, and was therefore removed with the excess of phenylhydrazine. According to Smith and Ransom, nearly pure β-phenylhydrazone is obtained by fusion of the calculated quantities of benzoïn and phenylhydrazine over a free flame. It is true that under these circumstances a certain amount of the pure β-body can be obtained from the first products of recrystallization, but the greater proportion consists of a mixture of the α- and β-varieties, melting at 103°–105°.[1] Such a substance, crystallizing in needles and fusing at 103°–105° can be obtained by bringing together the phenylhydrazones melting at 106° and 159°. In addition to the hydrazones, the product of direct fusion also contains a certain amount of unchanged benzoïn. The latter must be removed by treatment with cold ether, which leaves this body behind. If the substance is purified in this way and then recrystallized from alcohol, extraction of the crystals with acetic acid will take out the β-phenylhydrazone. The residue then, without recrystallization, melts at 156°–157° and consists of the α-variety. The same results are obtained by boiling an alcoholic solution of pure benzoïn with pure phenylhydrazine in a vessel connected with an inverted condenser for three and one-half hours. If the solution, which has then assumed a slightly yellow color, is allowed to stand, pure β-phenylhydrazone, completely soluble in acetic acid, at first separates. If the latter is filtered, and the mother-liquors diluted with water, the resulting crystalline precipitate melts at 103°–105°. This is a mixture of the α- and β-varieties. Extraction with glacial acetic acid and recrystallization of the insoluble remainder then leads to the pure α-hydrazone. This is, to the best of my knowledge, the best way to prepare α-benzoïnphenylhydrazone.

On page 115 of their article, Smith and Ransom state that β-benzoïnphenylhydrazone is converted into the α-body by

[1] The proportion of β to α is about 6 to 1.

boiling in alcoholic solution with two gram-molecules of phenylhydrazine, a 50 per cent. yield being obtained. On carefully repeating this experiment with pure β-benzoïnphenylhydrazone, I found that from 2 grams I could obtain only 0.05 gram of the α-modification, so that only a minimal quantity of the latter body is formed. Smith and Ransom's result, therefore, was due to the fact that they, in reality, were dealing with a mixture.

The Oxidation of β-Benzoïnphenylhydrazone.

It is impossible successfully to oxidize this substance by means of mercuric oxide in the cold, because the change takes place very slowly, if at all. Better results are obtained by passing nitrogen trioxide gas into the ethereal solution. This method has been used by Dr. Gomberg, of this laboratory, in converting benzenehydrazotriphenylmethane into benzeneazotriphenylmethane.

5 grams of pure β-benzoïnphenylhydrazone were dissolved in 100 cc. absolute ether, well cooled by means of a freezing-mixture, and nitrogen trioxide was then slowly passed in. The solution at once began to turn red, and the reaction is completed as soon as a somewhat greenish color becomes visible. The whole was then immediately extracted repeatedly with a dilute cold solution of potassium carbonate, by which means the ethereal solution finally changed to a thick mass of red, flaky needles. The operation was continued until the carbonate just began to assume a permanent reddish tint, a sign that the excess of trioxide had been removed. The supernatant ether, which contained the new body, was then separated and filtered. On drying the mother-liquors and evaporating *in vacuo*, a further quantity of the new body, in addition to benzoic aldehyde, could be obtained. In all there were formed 3.3 grams of the red crystals, 0.35 gram of benzoic aldehyde (determined as benzalphenylhydrazone, and representing 1.00 gram of the original body) and 0.7 gram of a non-crystallizable tar.

The substance formed by this reaction crystallizes from alcohol in large, red needles, melting at 137° with decompo-

sition and evolution of the red vapors of nitrogen trioxide. Treated with bromine, in chloroform solution, the body gives a fine, deep-yellow perbromide.

I. 0.1751 gram substance gave 0.3519 gram CO_2 and 0.0620 gram H_2O.

II. 0.2002 gram substance gave 0.3978 gram CO_2 and 0.682 gram H_2O.

III. 0.2101 gram substance gave 0.4196 gram CO_2 and 0.077 gram H_2O.

IV. 0.1551 gram substance gave 27 cc. nitrogen at 25° and 735 mm.

	Calculated for $C_{20}H_{18}N_4O_4$.	Found. I.	II.	III.	IV.
C	55.05	54.25	54.19	54.48	....
H	3.89	3.93	3.77	4.17	....
N	19.24	....	....	....	18.7

Another analysis of a product recrystallized from acetic ether, entirely in the cold, gave 55 per cent. carbon and 4.34 per cent. hydrogen. The analytical data were unfortunately lost. These numbers agree best with a body formed according to the following equation:

$$C_{20}H_{18}N_2O + 2N_2O_3 = C_{20}H_{16}N_4O_4 + H_2O.$$

If a direct addition of two molecules of nitrogen trioxide to one of the azo body had taken place, the product would have the formula, $C_{20}H_{18}N_6O_7$, which requires 52.86 per cent. carbon and 3.82 per cent. hydrogen. It is possible that a certain percentage of nitrogen trioxide is always separated on recrystallization, thereby increasing the numbers for carbon and hydrogen, but in view of the close concordance of results obtained from several recrystallizations, this does not seem likely.

A molecular weight determination was made, methyl oxalate being used as the solvent:

Methyl oxalate, 26,973. Depression, 0.135°.
Substance, 0.2198.
Calculated, 443; found, 320.

It is evident from this result that a certain amount of dissociation has taken place, a portion of the nitrogen trioxide having separated. This view is confirmed by the fact that if the solution is allowed to stand and the depression is deter-

mined from time to time, the latter constantly increases until the molecular weight 170 is reached, the calculated molecular weight, if complete separation into three molecules had taken place, would be 141. As to the constitution of this body, nothing definite can be said; most probably it is formed by addition of the oxide of nitrogen to the azo body, much in the same way as the perbromides are produced; that the original nitrogen atoms now possess the structure of an azo body is rendered extremely probable by the fact that this new substance takes up bromine to form a perbromide. The red needles dissolve in caustic potash with an intense purple color. If the solution is instantly acidified, the original body again separates; if it is allowed to stand, complete decomposition, with the formation of tarry products, sets in. Sodium carbonate, in aqueous sclution, has little effect. If alcohol is added, the same purple color appears. Boiling with phenylhydrazine in alcoholic solution seems to cause no change. When the body is dissolved in alcohol and reduced by means of sodium amalgam, large quantities of ammonia are formed, and the solution soon becomes colorless; water then throws down an amorphous, white body which, however, is extremely unstable, rapidly taking up oxygen from the air and forming a deep-red, non-crystallizable oil. If the solution is acidified and extracted with ether, and the latter evaporated, a tarry mass remains. As yet I have not succeeded in converting the red substance either into the corresponding azo body or into β-benzoïnphenylhydrazone. The solutions in methyl oxalate and in benzene are yellow, and not red, as would be expected. The constitution of this substance will be the subject of further investigation.

If the new body is dissolved in chloroform, and bromine, in excess, added, the latter is instantly taken up, without the evolution of hydrobromic acid. On evaporating the solvent, the entire residue changes to a mass of yellow crystals, which melt, after recrystallization from acetic ester, at 161°–162° with decomposition.

A bromine determination gave 34.7 per cent. bromine; calculated for $C_{30}H_{16}N_6O_6 + 3Br$ is 35.4. Carbon and hy-

drogen came somewhat too high for this formula, so that probably a portion of the oxide of nitrogen was driven off by the action of bromine, and this is rendered more probable by the fact that the analytical results vary with each recrystallization, so that it has as yet not been possible to obtain this substance in a state of purity. The figures demonstrate beyond a doubt, however, that the nitrogen trioxide is not to any extent expelled by the bromine, the latter simply adding itself. The appearance and properties of this perbromide are so closely like those of the others which have been described, that there seems little doubt as to the azo structure of the body which is the basis of the formation. The great stability of the addition-product is rather peculiar, but then the perbromides are equally stable. A further proof that the above view is correct is found in the fact that Gomberg, in oxidizing his benzenehydrazotriphenylmethane to benzeneazotriphenylmethane by the same method, obtained a product which on analysis always gave too high numbers for the nitrogen. This result is in all probability due to the formation of a certain proportion of a similar addition-product.

Similar results are obtained on treating ethylidenephenylhydrazone with nitrogen trioxide, and the resulting body, also, only retains a portion of the oxide. There seems to be no doubt, considering the above facts, that β-benzoïnphenylhydrazone has the structure represented by the formula,

$$\begin{array}{l} C_6H_5.C.OH \\ \quad\quad\| \\ C_6H_5.C.NH.NH.C_6H_5. \end{array}$$

The action of nitrogen trioxide on α-benzoïnphenylhydrazone takes place in an entirely different manner. One gram of the body was dissolved in absolute ether, cooled with a freezing-mixture, and nitrogen trioxide gas slowly run in. A white, crystalline precipitate instantly appeared, so that the liquid was soon changed to a thick paste. If the action is continued for too great a length of time, the quantity of this new body diminishes and the solution assumes a red color. This white substance is rapidly decomposed on exposure to the air. In order to isolate it, it was therefore filtered in a

Brühl apparatus in a current of carbon dioxide, washed with ether and, as soon as dry, treated with a cold solution of sodium carbonate. The latter reagent changes the body to a white, crystalline powder which separates from alcohol in needles, melting at 212° to 213°. The quantity at my disposal has heretofore been insufficient for the purposes of analysis. It is most probably the tetrazone, the original precipitate being the nitrite of that body. I was unable to obtain any of the red body derived from the β-hydrazone, on using the *pure* α-body, but I did observe its formation when using a sample prepared according to Smith and Ransom's directions. This result is probably due to the fact that some of the β-variety was present in the latter instance. γ-Benzoïnphenylhydrazine apparently does not react with nitrogen trioxide.

As a result of this investigation we must therefore accept the existence of three benzoïnphenylhydrazones, the low-melting individual exhibiting different chemical characteristics from the others, and, as was remarked above, it is probably the hydrazo-compound. The α- and γ-phenylhydrazones differ but little in their melting-points (3°), but do not resemble each other, either in appearance or solubility. This small distinction in the melting-points is entirely different from what would be expected if they were stereoisomers, such as the bodies described by Hantzsch and Krafft[1] and Hantzsch and Overton[2], for these substances all show a difference of 30°–50°. According to our present views, it is difficult to see what other distinction, excepting that of geometric isomerism, there can be between the two classes of phenylhydrazones described by Hantzsch, but the same also applies to α- and γ-benzoïnphenylhydrazones.[3] The interval between the melting-points of β- and α-benzoïnphenylhydrazones is 53°, and therefore almost the same as that in the case of the

[1] Ber. d. chem. Ges., **24**, 3525.

[2] *Ibid.*, **26**, 9; compare Wegscheider, Monatshefte f. Chem., **17**, 245.

[3] The structure $C_6H_5.C.OH$ / $C_6H_5.C.NH.N.C_6H_5$ (H) is also possible for γ-phenylhydrazone, but it is hardly probable.

bodies of Hantzsch, yet the substances certainly are distinct in their chemical behavior. In view of these considerations it is, therefore, desirable that this entire relationship should be subjected to further investigation.

Experiments with Fischer's two ethylidenephenylhydrazones[1] were also undertaken, but as in this case a body was formed which probably is a representative of a new class of substances, the nitrosophenylhydrazones, a detailed investigation was left for the future. A few results which have an immediate bearing on the present work, will, however, be detailed here.

Two grams of the β-phenylhydrazone, melting at 60°, were dissolved in ether, cooled in a freezing-mixture, and then nitrogen trioxide slowly added. A white precipitate appeared at once and the reaction was complete as soon as the solution had assumed a greenish tint. The resulting substance was then filtered off, and the ether repeatedly extracted with small quantities of dilute caustic potash until the latter retained its alkalinity. It was then dried over fused sodium sulphate and evaporated *in vacuo*, a yellow crystalline body remaining, which was purified by dissolving in alcohol and precipitating with water, when it was found to melt at 83°. The crystals behave very much like those of the red body derived from β-benzoïnphenylhydrazone; they decompose when heated, and give off nitrogen trioxide, not, however, in such quantity as does that substance. Bromine yields a characteristic perbromide, which decomposes when it is boiled with alcohol in the same way as do the others described above. The white precipitate, which at first separated, was filtered off, washed with ether and dried in a vacuum desiccator. When heated it explodes with the greatest violence; 0.05 gram, carefully heated in a test-tube, decomposed with a loud report and shattered the glass into powder. If this body is kept in a vacuum for any length of time, it gradually breaks down, turning red, and to a great extent loses its explosive property; the change is complete at the end of a week. This substance is probably the nitrosophenylhydra-

[1] Ber. d. chem. Ges., **29**, 793.

zone, and, as it had no direct bearing on the present work, it was reserved for future study.

β-Ethylidenephenylhydrazone (m. p. 60°) is readily oxidized by yellow oxide of mercury. If the substance is dissolved in ether, the reaction at once sets in at ordinary temperatures, and is complete in twelve hours. After filtering and evaporating *in vacuo*, a red oil is left, which contains a certain quantity of yellow crystals. The latter, when purified by means of ligroïn, melts at 80°, and their analysis and molecular weights proved them to be ethylidenephenylhydrazone. These crystals are not attacked by oxide of mercury in the cold, and they consist of the modification which Fischer supposed might be a mixture of the α- and β-bodies,[1] but which that investigator also considered as a possible third isomer. According to the above result they certainly could contain no β-body, for they were twice treated with an excess of mercuric oxide, so that Fischer's second supposition becomes more probable. This is further borne out by the fact that the body melting at 60° in part changes to that melting at 80° on standing in the cold. The oil which was formed during the oxidation reaction could not be crystallized. It was of a dark-red color and decomposed violently when it was heated. Bromine, in chloroform solution, instantly yielded a yellow, crystalline perbromide. According to the above, the β-phenylhydrazone is to be looked upon as the hydrazo body. α-Ethylidenephenylhydrazone, melting at 100°, does not reduce mercuric oxide in the cold in ethereal solution. It seems to be much more stable when exposed to the air, although the pure β-phenylhydrazone does not decompose rapidly under these conditions. Nitrogen trioxide converts it into the same white, explosive body as is obtained from the β-variety. The ethylidenephenylhydrazones, therefore, display the same relationships as the benzoïn derivatives, and, as in the case of the latter, there are probably three varieties. One marked difference must be noted, however,—the ethylidenephenylhydrazones are readily converted, the one into the other, the one melting at 60° into the one melting

[1] Ber. d. chem. Ges., **29**, 776.

at 80° on standing. The reverse reaction takes place on distilling the α-body; and the β-variety is changed to the α-variety, melting at 100°, by simply boiling for a short time with a dilute, alcoholic solution of caustic soda. It is for this reason that an investigation of these substances offers greater difficulties.

The Action of Phenylhydrazine on α-Halogen Substitution-products of the Ketones.

After Nef[1] had shown that the same body which Bender[2] obtained by treating α-chloracetoacetic ester with phenylhydrazine could also be prepared by the oxidation of the phenylhydrazone of acetoacetic ester by means of mercuric oxide, it seemed necessary to determine if other azo compounds could be prepared according to the same method, and to render the azo structure of benzeneazo-β-oxycrotonic acid more certain by means of their study. Hess[3] has already investigated the action of phenylhydrazine on bromacetophenone, obtaining a body which melts at 137°. To this he assigned the formula $CH_2(C:N.N.C_6H_5)C_6H_5$ as most probable. Accordingly this substance is an isomer of the azo body, $CH_2(=C.N.N.C_6H_5)C_6H_5$, which should be obtained by the oxidation of acetophenone. As I mentioned above, I could prepare the product only in the form of an oil, but the behavior of *p*-brombenzeneazo-*i*-styrene, which is crystalline, demonstrates at once that the substance of Hess cannot possibly be an azo body; it has too high a melting-point, and forms no perbromide; in fact, the action of bromine seems to produce a complete decomposition, yielding nothing but tarry products. A molecular weight determination showed that the body has not a simple structure.

[1] Am. Chem. (Liebig), **266**, 74. [2] Ber. d. Chem. Ges. **20**, 2747.
[3] Ann. Chem. (Liebig), **232**, 234.

Benzene, 27.227. Depression, 0.075.
Substance, 0.1521.
Calculated for $2C_{14}H_{13}N_3$, 418; found, 365.

As this result showed that the body obtained from bromacetophenone and phenylhydrazine was no azo substance, it was of no further interest to me; nevertheless I will describe a curious reaction which the substance undergoes. Hess's body is decomposed by dilute acids with extreme ease, and a peculiar change takes place. If the pure body is dissolved in warm glacial acetic acid, and then *promptly* precipitated with water, a new body separates in white needles; the greater part, however, remains in solution to be precipitated as an amorphous, brown powder, which could not be purified. If the substance is heated with alcohol and a drop of hydrochloric acid, in a sealed tube at 100° for two hours, there is slight pressure on opening and a little of an amorphous, brown precipitate has separated. If the latter is filtered and the solution evaporated in a vacuum, long, silky needles, melting at 114°–115°, separate. These are identical with those obtained from the solution in acetic acid. Even alcohol alone, without the addition of hydrochloric acid, is able to produce this change if the heating is carried on long enough. In this way I obtained 2 grams of the pure crystals from 7 grams of Hess's body; at the same time a considerable quantity of the brown, amorphous substance is always formed. Analysis of the substance melting at 114°–115° gave the following numbers:

I. 0.1410 gram substance gave 0.4368 gram CO_2, and 0.0755 H_2O.

II. 0.1638 gram substance gave 0.5036 gram CO_2, and 0.0907 H_2O.

III. 0.1361 gram substance gave 12 cc. nitrogen at 22° and 738 mm.

	Calculated for $C_{20}H_{18}N_2$.	Found. I.	II.	III.
C	83.91	84.46	83.84	....
H	6.29	5.95	6.15	....
N	9.78	....	....	9.82

The formula $C_{20}H_{18}N_2$ is that of the original body with the addition of C_6H_6 ($C_{14}H_{12}N_2 + C_6H_6 = C_{20}H_{18}N_2$),

and the properties of the substance, as well as the melting-point agree closely with those given for desoxybenzoïnphenylhydrazone,[1] but I did not prepare the latter body for comparison. Certainly, the formation of a substance having the formula $C_{20}H_{18}N_2$ from a substance produced from bromacetophenone and phenylhydrazine is curious. If it is desoxybenzoïnphenylhydrazone the change amounts to a substitution of phenyl for bromine. This reaction deserves further investigation, but as it had no immediate bearing on this work it was, for the present, set aside.[2]

If the body discovered by Hess is dissolved in ether, and dry hydrochloric acid is passed in, a white hydrochloride at once separates. The latter deliquesces in the air and quickly changes to a red, tarry substance. It is soluble in water and addition of alkalies precipitates the same non-crystallizable amorphous substance referred to above. If the hydrochloride is kept in a desiccator it loses a part of its acid and changes to a substance which is stable in the air. This body behaves in the same way when it is treated with alkalies. Benzoyl chloride and acetyl chloride produce crystalline bodies which apparently are identical with the stable hydrochloride. They yield the same amorphous substances when treated with caustic potash or soda and the same change takes place in the original substance if it is treated with the latter reagents. It is evident that Hess's body is very easily decomposed, but the nature of the products formed scarcely invites to further investigation.[3]

[1] Smith and Ransom (This JOURNAL, **16**, 111) give 116° as the melting-point of desoxybenzoïnphenylhydrazone, and the melting-point of my body is 115°.

[2] The decomposition described above causes trouble when the product of the action of phenylhydrazine on bromacetophenone is recrystallized from alcohol. It is always partly decomposed by the prolonged boiling necessary to dissolve it, and the decomposition-products are then contaminated with the amorphous substances referred to above. It is best to extract Hess's body three or four times with hot alcohol; the bright, yellow residue is sufficiently pure for further work.

[3] I have improved the method of preparing bromacetophenone as follows: Pure acetophenone is dissolved in pure carbon disulphide, well cooled in a freezing-mixture, and then the calculated quantity of bromine is gradually added, the whole being vigorously stirred, a current of carbon dioxide being passed through the solution in the meantime. This latter precaution is taken in order to remove excess of hydrobromic acid. After all bromine has been added, the solvent is evaporated by gentle heat, *in vacuo*, when the remainder separates as somewhat greenish crystals. The latter are then dissolved in alcohol, and water is added until a separation just begins. The flask is finally placed in a freezing-mixture until crystallization is complete. In order to avoid the intensely irritating odor of bromacetophenone, all of these operations should be carried out in the same vessel.

The Action of Phenylhydrazine on Chloraldehyde Hydrate.

The reaction takes place with explosive violence if no diluent is used. In order to obtain the best results, the following method was adopted: 10 grams of chloraldehyde hydrate were dissolved in 200 cc. of alcohol, well cooled, and then 2 gram-molecules of phenylhydrazine slowly added. After a few minutes a separation of phenylhydrazine hydrochloride begins, and finally yellow needles also appear. On standing over night, covered with snow, the whole solidifies to a thick paste. The whole is then filtered and pressed, and finally all traces of phenylhydrazine hydrochloride are removed by repeated trituration by water. The product is then washed with methyl alcohol, dried, and recrystallized from lukewarm alcohol, from which it separates in slightly yellow needles. It is finally dissolved in ether and crystallized *in vacuo*, when it forms colorless prisms, melting at 94°–95°.

I. 0.1761 gram gave 0.4503 gram CO_2, and 0.1034 gram H_2O.

II. 0.1972 gram gave 42 cc. nitrogen at 19°.5 and 734.5 mm.

	Calculated for $C_{14}H_{14}N_4$.	Found. I.	II.
C	70.00	69.73	....
H	6.66	6.52	....
N	23.33	....	23.66

A molecular weight determination was carried out in solution in benzene.

Benzene	29.2268		
Substance	I. 0.4500	Depression	I. 0.33
"	II. 0.7719	"	II. 0.545

Calculated 240; found I. 229; II. 231.

These results show that the body is the phenylhydrazide of the phenylhydrazone of oxyaldehyde

$$\begin{array}{l} H_2C.NH.NH.C_6H_5 \\ | \\ HC:N.NH.C_6H_5, \end{array}$$

so that no azo body has been produced.

If this phenylhydrazine compound is boiled with alcohol or

benzene, no rapid separation of crystals occurs on cooling, but gradually a mixture is formed which melts all the way from 95° to 110°. If the mother-liquors are either diluted with water, or evaporated, then there remain some sandy crystals, covered with a thick oil. If these crystals are spread on a porous plate and finally recrystallized from alcohol, they melt at 160°–161°, and have the same percentage composition as the original body. This substance is probably a polymeric form. If the mixture melting between 95° and 110° is slowly crystallized from ether, a small quantity of a body melting at 110° can be isolated, but the latter changes its melting-point with each recrystallization. Probably the same relationships obtain here as are found in the case of the ethylidene-phenylhydrazones. I have, however, not as yet been able to decide definitely whether there is a third isomeric body, in addition to those melting at 94°–95° and 160°–161° respectively. If the variety melting at 94°–95° is dissolved in alcohol and boiled with phenylhydrazine then, strange to say, no change takes place. If it is heated with pure ether in a sealed tube to 100° for two hours, the tube opens without pressure, and all of the crystals are dissolved. On evaporation a thick oil, permeated with crystals melting at 160°–161°, remains. It is evident that this body is therefore easily converted from one form into the other. Sodium amalgam, in alcoholic solution, reduces it readily, the resulting substance forming long, white needles, melting at 100°.

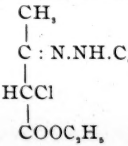
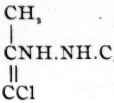
0.2155 gram substance gave 0.5519 gram CO_2, and 0.1397 gram H_2O.

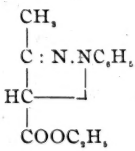
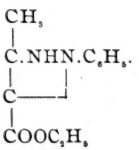
	Calculated for $C_{14}H_{18}N_4$.	Found.
C	69.40	69.39
H	7.46	7.20

This substance is therefore symmetrical ethylene-diphenylhydrazide, $\begin{matrix} CH_2NHNHC_6H_5 \\ | \\ CH_2NHNHC_6H_5 \end{matrix}$.

Bender[1] has studied the action of phenylhydrazine on brom- and chlorlaevulinic ester, on brombenzoylacetic ester and on

[1] Ber. d. chem. Ges., **21**, 2492.

chloracetone but in none of these cases did he obtain an azo body. The formation of benzeneazo-β-oxycrotonic ester from α-chloracetoacetic ester and phenylhydrazine is, therefore, a solitary instance, if the substance is really an azo body. It is, however, true that the same crystals are obtained by the action of mercuric oxide on the hydrazone of acetoacetic ester, but then, if the constitution assigned to it is really the correct one, a rearrangement of the atoms must have taken place in the case of Bender's synthesis, for an azo body cannot result from a substance of the structure,  or  , by means of a simple reaction. A more probable formula would seem to be

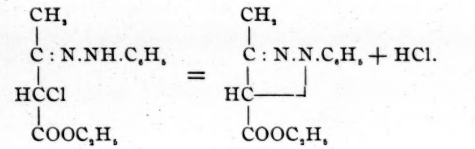
 or 

The substance has a simple molecular weight, for I found 206; calculated 218.

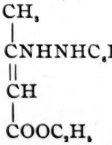
The following facts speak against the azo formula: The body melts quietly, without the evolution of a gas; decomposition sets in only considerably above the melting-point. Thiele has shown[1] that his aliphatic azo bodies always give off nitrogen quantitatively when heated above their melting-point, and the same is true of the azo substances described above. Bromine, in chloroform solution, does not give a perbromide,

[1] Ann. Chem. (Liebig), **290**, 33.

total decomposition resulting in the formation of a non-crystallizable tar taking place; the body is perfectly stable in the air, if it is in a pure state, while my similar bodies prepared from aliphatic phenylhydrazones are oxidized with explosive violence. The oxidation of the phenylhydrazone of acetoacetic ester by means of yellow oxide of mercury is by no means quantitative; phenylmethylpyrazolone can always be obtained from the alkaline extracts, and the ethereal solution deposits a considerable quantity of a thick oil, in addition to benzeneazo-β-oxycrotonic acid. It is scarcely justifiable to draw final conclusions as regards the constitution of the body from such insufficient data. It seems more probable, in view of the facts cited, that Bender's reaction takes place as follows:



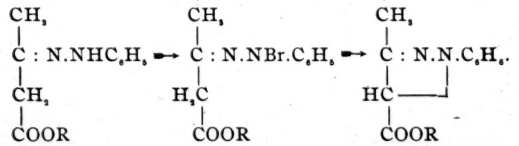
The phenylhydrazone of acetoacetic ester differs markedly in its behavior from the phenylhydrazones of acetone or acetophenone. If it is pure it is not oxidized by the air. 25 grams of the pure, recrystallized hydrazone were covered with petroleum ether and treated exactly as was acetone-p-bromphenylhydrazone. After four weeks there was little change. After three months the entire substance had changed to phenylmethylpyrazolone. If the phenylhydrazone of acetoacetic ester really has the structure



one would expect it to be oxidized in the air, just as the other compounds of similar constitution are. It is true that the oily or impure crystalline phenylhydrazone does change very rapidly when exposed to the action of the atmosphere, and it is not impossi-

ble that a small quantity of the hydrazo body is present in these preparations, but evidently this question is not easily decided experimentally.

Bromine, in ethereal solution, does not produce the *p*-compound from the phenylhydrazone of acetoacetic ester, as is the case with the other ketone phenylhydrazones. 6 grams of the crystallized phenylhydrazone of acetoacetic ester were dissolved in 100 cc. ether, and then, after cooling, 4.4 grams of bromine were slowly added. At first the bromine color instantly disappears; finally, however, after one-half has been added, the action becomes so slow that two to three hours are necessary to complete it. The ethereal solution is now colored deep-red and a black, tar-like substance has separated. The latter contained hydrobromic acid, but could not be crystallized. The ethereal solution was repeatedly extracted with 10 per cent. caustic potash and finally washed with dilute acids and water, dried over pure sodium sulphate and evaporated. By this method a small amount of a crystalline, red body can be isolated. The latter bears so close a resemblance to the substance discovered by Bender that it could easily be mistaken for it. It melts at 71°, however, and contains bromine; most probably it is the *p*-brom derivative of the body described as benzeneazo-*β*-oxycrotonic ester. The formation of this latter substance is much more readily understood if the hydrazone is not given the hydrazo structure: —

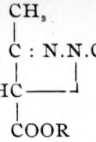


The last compound is then changed into the *p*-brominated body by the action of a further quantity of bromine; and this accounts for the fact that the reaction takes place more slowly toward the end.

In this connection it must be remembered that neither Bender nor Nef was able to reduce the benzeneazo-*β*-oxycro-

tonic ester back to the phenylhydrazone of acetoacetic ester; they always obtained phenylmethylpyrazolone or bisphenylmethylpyrazolone.

If the substance under discussion really has the structure



represented by the formula, $CH_3 \cdot C : N.N.C_6H_5$, HC, $COOR$, it would be expected that reactions which would split the ring could be discovered. Attempts in this direction have, as yet, led to no satisfactory result, because in every such attempt either noncrystallizable tars or derivatives of phenylmethylpyrazolone are formed.

The above considerations show that the azo structure for benzeneazo-β-oxycrotonic ester should by no means be taken for granted. On the other hand, this constitution is not disproved, except by negative testimony.

In conclusion, I wish to return hearty thanks to Messrs. Whitsit and Briggs, and to Dr. P. L. Sherman for their continued and ready assistance in this work.

ANN ARBOR, August, 1898.

Contributions from the Chemical Laboratory of the University of California.

NOTE ON THE ACTION OF LIQUID HYDRIODIC ACID ON ETHYL ETHER.

BY F. G. COTTRELL AND ROY RAVONE ROGERS.

Some time ago, while examining the properties of liquid hydriodic acid,[1] it was noted that when the acid was mixed with ether a vigorous action occurred, the temperature rising rapidly, the mixture, which at first appeared to be homogeneous, separated into two layers, one of which was assumed to be ethyl iodide, judging from its appearance and odor, and the other was assumed to be water and the excess of acid. No attempt was made at the time to separate and purify the product, or to determine the yield. The following supplements the previous work in this particular.

[1] Norris and Cottrell: This JOURNAL, **18**, 103 (1896).

The hydriodic acid was prepared and dried according to the method described in the previous paper.[1] The ether was prepared by washing commercial ether with a considerable volume of water, digesting with quicklime for a few days and distilling from the same. This was again distilled and then gave a boiling-point constant within a tenth of a degree.

After several preliminary experiments the following form of apparatus was adopted. We believe it will be found a very convenient form for reactions which are to be carried out under pressure.

The sealed end of a straight eudiometer-tube provided with a glass stop-cock was cut off and a smaller tube, sealed at one end, introduced into it, open end first. The cut end of the large tube was then sealed, thus providing a vessel of two chambers, into each of which liquids could be introduced through the stop-cock.

The whole apparatus was now weighed, the tube was then surrounded with solid carbon dioxide and gaseous hydriodic acid conducted by means of a narrow delivery-tube to the bottom of the eudiometer-tube, where it condensed to a liquid surrounding the inner tube. When about 15 cc. of this liquid had been collected, the delivery tube was withdrawn and the acid cooled until it solidified. Then a weighed amount of ether was run into the inner tube, and the stopcock closed and tied in securely.

The apparatus was now tipped slightly so that the ether mixed in small quantities at a time with the acid. The ether on coming in contact with the solid acid produced a vigorous reaction. The latter melted rapidly, even while surrounded by the solid carbon dioxide. If the ether and acid are suddenly mixed the temperature will rise from the freezing-point of the acid ($-55°$ C.) to at least $+40°$ or 50°. When mixing was complete the whole apparatus was weighed to determine the weight of acid used.

During the mixing the products began to separate into two layers. The tube was set aside for a week in a dark place average temperature about 18°), at the end of which time

[1] *Loc. cit.*

the heavier of the two layers had relatively increased in volume. After being cooled down somewhat, the tube was opened. Water was added, which mixed with the upper layer, but would not mix with the lower. The lower layer was washed with water, then with a little weak solution of caustic potash, dried over calcium chloride, and distilled twice. The following are the numerical data:

	Grams.
Weight of ether used	8.91
Weight of acid used	42.30

This is 1.33 times the quantity of acid required by theory for the reaction:

$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O.$$

Weight of crude product after washing with water, 35 grams; this is 94 per cent. of the quantity required by theory.

Weight of product after first distillation, 32.8 grams, which is 88 per cent. of the quantity required by theory.

After the second distillation the whole of the material boiled between 71.9° and 72° under 756 mm. pressure. The boiling-point of ethyl iodide, given by different authorities,[1] ranges about a degree on each side of this. Its specific gravity at 18° referred to water at the same temperature was found to be 1.941. Hagen gives 1.935 at 20°, and Linnemann 1.944 at 14.5°.[2] Its refractive index for the *D* line was 1.5133 at 18.5°. Hagen[3] gives 1.5131 at 20°.

Silva[4] found that when gaseous hydriodic acid reacted on methyl ether at 0° to 4°, the whole of the ether was converted into methyl iodide. With ethyl ether, on the contrary, only part was converted into iodide and part into alcohol; and the same was true for the higher ethers. No quantitative data are given.

The formation of water by the reaction itself in such cases as the above, soon establishes the same condition as when using a concentrated aqueous solution of the acid. It would be interesting to study the behavior of the anhydrous acid in

[1] Landolt and Börnstein: Chem. Phys. Tab. 1894, p. 65.
[2] *Loc. cit.* [3] *Loc. cit.* p. 427.
[4] Compt. rend., **81**, 323 (1875).

reactions where no water can form; *e. g.*, in the addition of hydrogen to benzene (Cf. Berthelot).[1]

It seems not improbable from the rapid and widespread increase in our facilities for liquefying and handling considerable quantities of gases that this method of applying such reagents as chlorine, sulphur dioxide, and ammonia may eventually come into quite general use. It has the great advantage of permitting a high concentration of the reagent without the necessity of introducing water or other solvents, while its practical application is by no means as difficult as might at first be supposed.

BERKELEY, CAL., Sept., 1898.

CONTRIBUTIONS TO OUR KNOWLEDGE OF THE OIL OF LEMON-GRASS.[2]

BY WILH. STIEHL.

The question in regard to the composition of the oil of lemon-grass has of late become of special interest, on account of the relations between the aliphatic aldehydes, $C_{10}H_{18}O$, (or their condensation-products with acetone) contained in them, and the ketones, $C_{13}H_{22}O$, obtained from violets.

Oil of lemon-grass or Indian oil of verbena is, as is well known, obtained by distillation of a species of grass, *Andropogon citratus*, in British India, Ceylon, Singapore, and Java, and is there sold in original packages to the European importers.

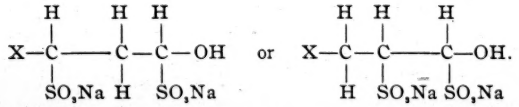
Messrs. Ph. Barbier and L. Bouveault deserve special mention for their excellent work in the investigation of the constituents of the oil of lemon-grass. Schimmel & Co., of Leipsic, have put on the market, under the name of "citral," an inactive aldehyde, $C_{10}H_{18}O$, obtained from oil of lemon-grass, without, however, stating how it is isolated and without carefully investigating it. F. D. Dodge[3] first described a method for the isolation of a characteristic aldehyde, $C_{10}H_{18}O$, from oil of lemon-grass. He shook the oil with a warm solution of sodium bisulphite, and in a short time obtained a solid bisul-

[1] J. prakt. Chem., **104**, 106 (1668).
[2] Communicated by the Author in MS. in German.
[3] This JOURNAL, **12**, 555.

phite compound. In a few hours this became liquid again, and there were thus obtained an aqueous liquid and an oil floating upon this. Dodge did not further investigate the oil. He treated the aqueous solution with caustic soda, and obtained a substance, $C_{10}H_{16}O$, which he investigated, and, after identification, called "citriodoric aldehyde." On the other hand, he evaporated the aqueous solution containing the aldehyde and bisulphite, and obtained from it beautiful crystals an inch in length, which had the composition $C_{10}H_{18}O{:}2NaHSO_3 + 4Na_2SO_3 + 50H_2O$. These gave citriodoric aldehyde with caustic soda.

Dodge properly drew the conclusion that the bisulphite compound of citriodoric aldehyde conducts itself quite differently from the typical compounds of the aldehydes with bisulphite. Dodge himself sums up his further investigation by saying that oil of lemon-grass contains an aliphatic aldehyde, $C_{10}H_{18}O$, with two ethylene bonds, which can easily be converted into cymene.

It may here be mentioned that Fr. Heusler[1] has observed a similar behavior in the case of the bisulphite compound of cinnamic aldehyde, and from the water solution has isolated the compound, $C_6H_5.C_2H_3(SO_3Na)CH(OH)(SO_3Na)$. From this compound, or its solution in water, cinnamic aldehyde can be separated only by means of caustic alkalies. This behavior is perhaps connected with the presence of the group X—CH : CH.CHO, and the formation of the soluble bisulphite compound may take place in either of the two ways indicated below:



According to this view citriodoric aldehyde must be C_7H_{13}. CH : CH.CHO, analogous to cinnamic aldehyde, C_6H_5.CH : CH.CHO.

Then W. Semmler[2] investigated the citral which Schimmel

[1] Ber. d. chem. Ges., **34**, 1805. [2] *Ibid.*, **34**, 201–211.

& Co. put on the market, and declared it to be identical with the geranial obtained by him by oxidizing "geraniol" so that the two expressions have been used since that time to designate one and the same substance.

Further, R. Hefelmann[1] made a quantitative estimation of geranial in oil of lemon-grass free from terpenes, and succeeded by means of bisulphite in isolating 13 per cent. of an aldehyde identical with geranial. Ferd. Tiemann and W. Semmler[2] have also worked on geranial and citral in their investigations on irone and ionone, and state that citral can be separated from oil of lemon-grass by means of the easily crystallized compound with sodium bisulphite, and that the compound of geranial and bisulphite in contact with the liquid from which it is formed passes into solution if the temperature is not too low, but that the aldehyde cannot be separated either by alkali carbonates or by caustic alkalies, as the sodium salt of a true sulphonic acid is formed.

This is a different behavior from that observed by Dodge[3] in the case of citriodoric aldehyde, and is more like that of the typical compounds of aldehydes with bisulphite. Accordingly, geranial (citral) cannot contain the group X—CH : CH.CHO, but must contain this, X—CH_2.CH_2—CHO.

It is clear, therefore, that up to the present two aldehydes of the formula $C_{10}H_{16}O$ have been shown to be present in oil of lemon-grass; *viz.*, Dodge's citriodoric aldehyde, C_7H_{11}. CH : CH.CHO, and Semmler's geranial (citral), C_7H_{11}.CH_2. CH_2.CHO.

The formula proposed by F. Tiemann and W. Semmler for geranial cannot be correct, for the different conduct of citriodoric aldehyde and citral towards sodium bisulphite cannot be explained by means of it.

Next, O. Doebner[4] applied his synthesis of α-alkyl-β-naphthocinchoninic acids from aldehydes, pyroracemic acid and β-naphthylamine to the terpene aldehydes, and describes α-citronellal-β-naphthocinchoninic acid melting at 225° and α-citral-β-naphthocinchoninic acid melting at 197°.

[1] Chem. Centralblatt, **64**, (I) 45 (1894).
[2] Ber. d. chem. Ges., **26**, 2708–2729.
[3] This JOURNAL, **12**, 553–564.
[4] *Ibid.*, **27**, 2020–2030.

Döbner tries at first to use this synthesis for the quantitative estimation of aldehydes in natural ethereal oils, but his efforts are unsuccessful, first, because the reaction does not take place quantitatively, and secondly, because an excess of pyroracemic acid and β-naphthylamine causes the formation of α-methyl-β-naphthocinchoninic acid, which remains mixed with the corresponding β-naphthocinchoninic acid. In an attempt to apply his reaction directly to oil of lemons, Doebner finds in this oil about 8 per cent. of aldehydes, consisting of about 25 per cent. citral and 75 per cent. citronellal.

Later, Ph. Barbier and L. Bouveault[1] show that oil of lemons contains no citronellal, $C_{10}H_{18}O$, but that it does contain dextro-licarhodal, $C_{10}H_{16}O$.

In the meantime Ph. Barbier and L. Bouveault[1] published their careful investigations on the constituents of oil of lemon-grass, and I give here a brief résumé of these.

They confirm Dodge's discovery[2] of citriodoric aldehyde in oil of lemon-grass. To obtain this aldehyde, they distilled five times under diminished pressure very carefully a sufficient quantity of the oil of lemon-grass and obtained the following three principal fractions:

I. 65°–75° under 12 mm. pressure (170°–175° at ordinary pressure).

II. 110°–115° under 12 mm. pressure (citriodoric aldehyde).

III. Above 115° under 12 mm. pressure (residue not investigated).

In fraction I. they found, besides a terpene (probably limonene), principally methylheptenone, $C_8H_{14}O$, for which they propose the formula, $CH_3—C(CH_3)=CH—CH_2—CH_2—CO—CH_3$, to account for the products of oxidation.

In fraction II. the citriodoric aldehyde of Dodge must be contained. As meanwhile the papers of Tiemann and Semmler on geranial and citral from oil of lemon-grass appeared, and as it seemed not improbable that geranial and citriodoric aldehyde might be identical, Ph. Barbier and L. Bouveault[3] tested the formula which was proposed by Tie-

[1] Compt. rend., **118**, 953–986, 1050–1052; **121**, 1159–1162; **122**, 84–86, 393–395, 1422–1424.
[2] This JOURNAL, **12**, 553.
[3] Compt. rend., **118**, 953–986, 1050–1052.

mann for geranial. They found that this could not possibly be the formula of their citriodoric aldehyde, and therefore they gave this another formula, which accounted for the products of decomposition.

In order to learn more about this interesting compound, and to continue further their investigations on the aldehydes, $C_{10}H_{16}O$, obtained from the alcohols, $C_{10}H_{18}O$, they compared the former with the aldehyde contained in oil of lemon-grass. For this purpose they studied the semi-carbazones[1] of these aldehydes exhaustively.

They again carefully distilled the above fraction II. in a vacuum with the aid of a column-still attachment, and separated it into the following fractions:

I. 107°–110° under 10 mm. pressure.

II. 110°–112° under 10 mm. pressure.

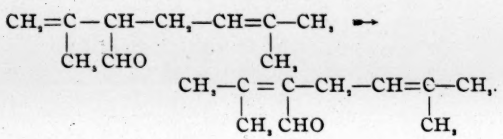
On crystallizing the semi-carbazones of these two fractions they obtained from both three different semi-carbazones melting at 171°, 160°, and 135°. They then prove in an elegant manner that the isomerism of these three semi-carbazones cannot be referred to the nitrogen, as they can all be converted into one semi-carbazone melting at 135°.

They say further: "Il n'existe pas dans l'essence de Lémongras d'aldéhyde répondant à la formule $C_{10}H_{18}O$, car il ne se forme pas de semi-carbazones autre que celles que nous venons de décrire." For two of the three aldehydes, $C_{10}H_{16}O$, they propose formulas, and call one "aldéhyde instable" and the other "aldéhyde stable." They also formulate their easy conversion into cymene.

In a later article:[2] "Sur les aldéhydes dérivées des alcools $C_{10}H_{18}O$ isomériques" they complete their investigations and prove that the semi-carbazone melting at 171° belongs to licarhodal, and that this under the influence of sulphuric acid passes into lemonal, as they call the aldehyde, $C_{10}H_{16}O$, which yields a semi-carbazone melting at 135°.

The conversion of licarhodal into lemonal they represent as analogous to the conversion of eugenol into isoeugenol, of safrol into isosafrol, and of estragol into anethol as follows:

[1] Compt. rend., **121**, 1159–1162. [2] *Ibid.*, **122**, 84–86.



In connection with this subject they say : "La transformation du licarhodal en lémonal n'est pas réversible, et le licarhodal, qui se recontre dans les produits d'oxydation du lémonal naturel (géraniol) de l'essence d'Andropogon schœnanthus provient du licarhodol gauche dans cette essence."

They have further investigated the citral from oil of lemons, and found that three aldehydes, $C_{10}H_{16}O$, occur in it, whose semi-carbazones melt at 171°, 160°, and 135°, and they remark : " Le citral de l'essence de citron ne contient donc pas de citronellal et la combinaison naphtocinchonique décrite par M. Doebner comme dérivant du citronellal et sans doute celle qui correspond au licarhodal."

It will be seen, therefore, that according to Barbier and Bouveault citronellel, $C_{10}H_{18}O$, cannot be contained either in oil of lemon-grass or in oil of lemons. In addition to the inactive aldehydes, $C_{10}H_{18}O$, geranial (citral) and citriodoric aldehyde, there is, however, an inactive aldehyde, $C_{10}H_{16}O$, laevolicarhodal contained in the oil. The detection and isolation of these aldehydes are difficult because, under the influence of acid reagents, they are transformed into the most stable inactive compound.

In a still later communication[1] these investigators give additional evidence of the existence of the three aldehydes, $C_{10}H_{16}O$, in oil of lemon grass, and propose for one of these, lemonal, the following formula :

Their parallel investigations of the alcohols, $C_{10}H_{18}O$, I can only mention here.

Recently F. Tiemann[2] has again published the results of

[1] Compt. rend., 122, 842-844. [2] Ber. d. chem. Ges., 31, 820.

his investigations on the constitution and the chemical conduct of geranial (citral) without, however, saying much that is new. He mentions among other things the splitting of citral into acetic aldehyde and methylheptenone by means of a solution of potassium carbonate which was effected by A. Verley, and recommends Doebner's α-citryl-β-naphthocinchoninic acid (of melting-point 197°) as a means of detecting and characterizing citral.

On the other hand, I cannot accept Tiemann and Krüger's proof that only geranial is contained in the oil of lemon-grass, and that its semi-carbazone can be resolved into isomeric substances that melt between 130° and 171°. On the contrary, on the basis of my experiments, an account of which is given below, I can fully confirm the statement of Ph. Barbier and L. Bouveault, for perfectly pure inactive citral (geranial) never gives a semi-carbazone melting at 171°, as O. Wallach and W. Naschold[1] have also found.

Notwithstanding the fact that Ph. Barbier and L. Bouveault have fully established the presence of three aldehydes, $C_{10}H_{16}O$, in oil of lemon-grass, and that these investigators have just as certainly proved the absence of citronellal from oil of lemon-grass as well as from oil of lemons, the following passage, nevertheless, occurs in this article: "Citral ist bislang der einzige Terpenaldehyd, von der Formel $C_{10}H_{16}O$, welcher in ätherischen Oelen nachgewiesen worden ist. Neben demselben tritt nur sein Dihydroderivat, das Citronellal zuweilen unter den Produkten des pflanzlichen Stoffwechsels auf. O. Doebner hat auf diesen Thatbestand zuerst aufmerksam gemacht, und auch angegeben, wie man Citronellal neben Citral nachweisen kann."[1]

In this article F. Tiemann also states that the condensation of geranial with acetone, according to Claisen, furnishes an excellent method for detecting and sharply characterizing this aldehyde, $C_{10}H_{16}O$, in the form of pseudoionone, provided

[1] Ber. d. chem. Ges., **31**, 822. In spite of the work of Barbier and Bouveault, O. Doebner (Ber. d. chem. Ges., **31**, 1891) recently expresses the opinion that citronellal is contained in oil of lemon-grass. This, as well as other errors in Doebner's article, is sufficiently explained by the work described in the present communication so that the work of Doebner, which only came to my knowledge after I had completed the preparation of this article, is refuted by the latter. I shall, in another place, return to the numerous contradictory statements of Doebner.

secondary reactions are avoided. He describes a method of procedure for this general method, by means of which geranial can be detected in oil of lemon-grass with ease. I have also been led, independently of F. Tiemann, to this excellent method of detecting the aldehydes, $C_{10}H_{18}O$, in the ethereal oils, and can confirm the statement that pseudoionone is always obtained, whenever geranial or citral is contained in the original material. For this reason I have made this method, the application of which I shall describe farther on, the foundation of my investigation of the oil of lemon-grass.

As the condensation of the whole of the aldehyde contained in natural oil of lemon-grass with acetone gave me a mixture of aldehyde-acetone condensation-products, in which I could, to be sure, detect Tiemann's pseudoionone, but from which I could not isolate it in pure condition, I decided to separate the aldehydes, the presence of which had been shown by the previous investigations of Dodge, Barbier and Bouveault, and Tiemann and Semmler.

I. *Investigation of Oil of Lemon-grass.*

Large quantities of directly imported, unadulterated oil of lemon-grass were well mixed, and in portions of 50 kilograms carefully separated by water-vapor in an apparatus fitted with a column-still attachment into fractions of 2–2½ kilograms.

A.

20 fractions of 50 kg.

I.	α_D for 1 dm.	= +	10°51′
IV.	" " "	= +	7°45′
VII.	" " "	= +	0°41
IX.	" " "	= —	0°40′
XIII.	" " "	= —	1°0′
XVII.	" " "	= —	1°30′
XX.	" " "	= —	2°5′

B.

25 fractions of 50 kg.

I.	α_D for 1 dm.	= —	23°0′
III.	" " "	= —	15°15′
X.	" " "	= —	1°13′
XIII.	" " "	= —	0°50′
XVII.	" " "	= —	1°45′
XXII.	" " "	= —	2°45′
XXV.	" " "	= —	2°50′

I have here given the results of these two distillations for the reason that they show that oil of lemon-grass from different sources sometimes contains dextro-rotatory, sometimes laevo-rotatory, hydrocarbons, and that the less volatile active aldehydes are always laevo-rotatory, as I shall show later. A transition from active terpenes through inactive aldehydes to active aldehydes, therefore, takes place.

From the first fractions, besides cymene, which is probably formed by elimination of water from the aldehydes, $C_{10}H_{18}O$, only limonene and dipentene could be isolated, the latter being characterized by means of its bromide melting at 126°.

Thereupon geraniol and citronellal were sought for in the fractions, but neither was found in the oils examined by me.

The other fractions of the oil of lemon-grass were then subjected to careful, repeated fractionations under diminished pressure and divided into the following principal fractions:

Fraction.	*A.*	*B.*	*C.*
Boiling pt. 12 mm.	106–108°	117–120°	126–135°
" " 760 "	226–229°	133–137°	240–245°
Density at 20° D =	0.8928	0.9020	0.8980
Refract. at 20° n_D =	1.48451	1.48905	1.48050
Rotation in 1 dm. tube α_D	$-\frac{1}{2}°$	$-5°6'$	$-10\frac{1}{2}°$

As the α-citryl-β-naphthocinchoninic acid melting at 197° is especially characteristic of geranial (citral), I prepared the naphthocinchoninic acid compounds of the above fractions according to O. Doebner's directions, and obtained the following results:

Fraction *A* contains only very small quantities of geranial; for the melting-point of the naphtocinchoninic acid prepared from it ranges from 197° to 205°, and the acid can be separated into (*a*) a difficultly soluble portion melting at 197°, and (*b*) an easily soluble portion melting at 204°–205°.

Fraction *B* contains no geranial and gives the following two naphthocinchoninic acids: (*a*) a difficultly soluble one melting at 205°, and (*b*) an easily soluble one melting at 229°.

Finally, fraction *C* gives only one naphthocinchoninic acid, and this melts at 244°–246°.

It will be seen from the results of the methodical fractiona-

tion of natural oil of lemon-grass, that several aldehydes must be present in it, as several easily distinguished α-alkyl-β-naphthocinchoninic acids were obtained, and that even a carefully distilled oil of lemon-grass (citral commercielle[1]) can never be claimed to be citral (geranial).

As no homogenous substances can be obtained by distillation, I have been obliged to seek for other methods of separation.

II. *Separation of the Aldehydes of Oil of Lemon-grass by means of Sodium Bisulphite.*

In order, at the outset, to exclude all terpenes and other substances that are not aldehydes (methylheptenone was not present in the oil worked up by me), I separated the aldehydes of oil of lemon-grass by means of sodium bisulphite as follows:

10 kilograms of fine oil of lemon-grass, 20 kilograms of a 35 per cent. solution of sodium bisulphite, and 10 kilograms of ice were stirred together until the solid bisulphite compound was formed, then this was at once filtered cold by means of a pump, well washed out, and pressed to hard cakes in a well-cooled press. These cakes were then broken up in ice-water and decomposed by stirring them with a solution of sodium carbonate. The oil thus obtained was carefully washed and rectified with water-vapor or in a vacuum. The mixture of aldehydes had the following properties:

Boiling-point 106°–128° under 12 mm. pressure;
225°–243° " 758 " "
Density 0.8887 at 20°;
Refraction $n_D = 1.48306$ at 20°;
Rotation $\alpha_D = -4° 13'$ at 20° in a 1 dm. tube.

A mixture of aldehydes having the above properties was called "citral," because it was obtained from oil of lemon-grass through the pure double compound with sodium bisulphite. But this is absolutely inadmissible, as citral (geranial) in the first place is optically inactive, and, further, it has a sharp, constant boiling-point and other well-marked properties.

[1] This expression has been introduced by a French firm.

By fractionating this mixture I then obtained almost exactly the same fractions that I obtained from oil of lemongrass and designated as *A*, *B*, and *C*; and these gave entirely similar α-alkyl-β-napthocinchoninic acids. Besides these I obtained a portion boiling at 140°–145° under 12 mm. pressure, which showed a rotation of $\alpha_D = -26°$ in a 100 mm. tube, gave a naphthocinchoninic acid melting at 251°–252°, and had markedly the odor of cedar wood.

As I could not obtain pure geranial (citral) in this way, I made it by oxidation of geraniol which had been purified with the aid of its compound with calcium chloride according to the method of W. Semmler.[1] The geranial (citral) purified through the bisulphite compound had the following physical properties:

Boiling-point: 111°–112° under 12 mm. pressure;
" 214°–227° " 760 " "
Density: 0.8898 at 20°;
Refraction: $n_D = 1.48752$ at 20°;
Rotation: $\alpha_D = \pm 0°$ (inactive).

This is therefore undoubtedly the geranial (citral) of Tiemann and Semmler. The melting-point of the naphthocinchoninic acid is 197°.

As Tiemann and Semmler[2] have called attention to a peculiar behavior of the bisulphite compound of citral on standing longer than twenty-four hours in the liquid in which it is formed, and as Dodge[3] had previously observed a no less peculiar behavior of the bisulphite compound of citriodoric aldehyde under the same conditions, which was entirely different from that of the citral bisulphite, I first performed the following experiments: On the one hand I shook one part geranial, and, on the other hand, one part of the above mixture of aldehydes with two parts of a 35 per cent. solution of bisulphite, and two parts water until the solid bisulphite compound was formed. During the stage of formation no difference between the two cases was observed. The two masses were then allowed to stand. After the lapse of an hour the bisulphite compound of the aldehydes from oil of lemon-grass be-

[1] Ber. d. chem. Ges., **23**, 2965; **24**, 201; **26**, 2708.
[2] *Ibid.*, **26**, 2708.
[3] This JOURNAL, **12**, 553–564.

gan to liquefy and became markedly warm, while the compound of geranial remained solid. After a time the bisulphite compound of the aldehyde of lemon-grass was decomposed, with the exception of a small residue of little leaf-like crystals, into an oil and a clear aqueous solution with an alkaline reaction. This geranial bisulphite, which was at first granular, had become converted into beautiful laminae of a silken lustre in twenty-four hours. The small quantity of aqueous liquid that separated during this time still retained an acid reaction.

Thereupon I repeated these experiments, and warmed the bisulphite compounds in their mother-liquors about a quarter of an hour in a boiling water-bath, and then found that both had become liquid, but from the bisulphite compound from oil of lemon-grass an oil had separated, which was not the case with the geranial bisulphite.

I then carefully cooled both, when the geranial bisulphite crystallized out, but the bisulphite compound from the oil of lemon-grass did not. I then separated the oil from the latter, and filtered the aqueous solution from the former. I then extracted both aqueous solutions with ether and treated them with sodium bicarbonate. In neither case did I observe any separation at all. I then added caustic soda to both, and obtained from the solution of the aldehydes of the oil of lemon-grass an abundant yield of oil, while the bisulphite solution of the geranial gave nothing. This caused me to repeat the experiments of F. D. Dodge,[1] and of Tiemann and Semmler.[2] For the preparation of citriodoric aldehyde, according to Dodge, one kilogram of the above mixture of aldehydes of natural oil of lemon-grass was shaken with two kilograms of the solution of commercial sodium bisulphite, and two kilograms of water, at the ordinary temperature, until a bisulphite compound was formed which caused the entire mass to solidify, and then this was further shaken until it became liquid again. In this way an oil floating upon the surface was obtained and an aqueous clear solution. The oil was separated and placed aside, while the aqueous solution was

[1] This JOURNAL, **12**, 553. [2] Ber. d. chem. Ges., **26**, 2709; **24**, 203; **31**, 820.

digested with sodium bicarbonate at 40°–50°, and then extracted with ether. The aqueous solution after treatment with ether was shaken with concentrated caustic soda in the cold. The oil, which separated in large quantities, was well washed and rectified with water-vapor or in a vacuum. In this way the perfectly inactive citriodoric aldehyde of F. D. Dodge was obtained.

On the other hand, I also attempted the preparation of citral (geranial) according to the directions of F. Tiemann and W. Semmler, and I observed that, in the first place, the geranial bisulphite also dissolves if allowed to stand for some time in the liquid in which it is formed, and that after this it cannot be regenerated by caustic soda; and that, in the second place, a sufficient quantity of a strongly acid solution of sodium bisulphite must be used in order that geranial (citral) may be formed from the natural aldehydes of lemon-grass under the transforming influence of sulphurous acid. Therefore each portion of one kilogram of the mixed aldehydes of the oil of lemon-grass was thoroughly shaken with four kilograms sodium bisulphite and two kilograms water until the bisulphite compound was formed. The temperature was then raised to 40°–50°, then again cooled, and then allowed to stand in a cool place for twenty-four hours. The beautifully crystallized geranial bisulphite was then drawn off, by means of a pump, from the aqueous solution and the accompanying oil, or separated from them by careful washing with alcohol and ether. The geranial bisulphite was then decomposed at a low temperature by means of sodium carbonate. The product obtained is the citral of Tiemann and Semmler, which, I have convinced myself, is identical with the geranial from geraniol. It should be mentioned that, after the digestion with sodium carbonate at 40°–50°, and after the subsequent extraction with ether, I separated the citriodoric aldehyde from the aqueous solution by means of caustic soda.

The analyses and constants of geranial are given in the table farther on.

Finally, I sought for the laevo-licarhodal which was pre-

pared by Barbier and Bouveault[1] by the aid of its semicarbazone melting at 171°, and I found that this compound was contained in the oil that was set aside in the course of the preparation of citriodoric aldehyde and of geranial. I have called this aldehyde allo-lemonal and have separated it by the following method by means of sodium bisulphite directly from oil of lemon-grass.

The conditions may be so chosen that the citriodoric aldehyde passes into solution in the form of the bisulphite compound which can be decomposed only by caustic soda; the geranial dissolves as a sulphonic acid which cannot be regenerated, while the bisulphite compound of allo-lemonal decomposes, yielding allo-lemonal; or the conditions may be so chosen that citriodoric aldehyde remains in solution, geranial being present at the same time in the form of a solid bisulphite compound, and allo-lemonal as an oil, under which circumstances they can be separated.

One kilogram of the mixed aldehydes of oil of lemon-grass was shaken with two kilograms sodium bisulphite and two kilograms water, until a solid bisulphite compound was formed, and then immediately shaken further until solution or decomposition of this compound was brought about. In consequence of the great heat of reaction which is evolved in the formation of the soluble bisulphite compound of citriodoric aldehyde, $C_{10}H_{18}O.2NaHSO_3$, any geranial which was present remained dissolved as sulphonic acid, while the allo-lemonal separated. At this temperature the allo-lemonal is reduced to a considerable extent to allo-lemonol by the action of the sulphurous acid, while geranial and citriodoric aldehyde do not suffer this change. Therefore, 250 grams of the crude allo-lemonal were shaken with 500 grams sodium bisulphite and 500 grams water until the solid bisulphite compound was formed, then well cooled, and the solid compound drawn off by means of a pump, and washed with alcohol and ether. The bisulphite compound of allo-lemonal is now added either to a cold dilute solution of sodium carbonate or to pure warm water, when pure allo-lemonal separates easily, and can be rectified

[1] Compt. rend., **122**, 84-86.

either in steam or under diminished pressure. The aldehyde obtained in this way is optically active, and according to the analyses and determination of its molecular weight it has the formula $C_{10}H_{16}O$. It is the laevo-licarhodal of Barbier.

The physical constants and the conduct towards bisulphite I have given in the table which will be found farther on.

Barbier and Bouveault carried out their beautiful investigations on the aldehydes of the oil of lemon-grass with the aid of their semicarbazones; and although O. Wallach and W. Naschold[1] have shown that many of these occur in two isomeric forms, comparable results must be obtained in working according to one and the same method under definite conditions. Therefore, we convert our three aldehydes, citriodoric aldehyde, geranial, and allo-lemonal, into semicarbazones according to the following method:

A solution of semicarbazide was prepared according to the directions of Thiele and Stange[2] from 130 grams hydrazine sulphate, 55 grams sodium carbonate, 85 grams sodium cyanate, and 1000 cc. water. This solution, in portions of 100 cc., was treated with 150 cc. alcohol, filtered after standing for several hours, and 10 grams of the aldehyde added to the clear solution. After some time the separation of the semicarbazone began and in twenty-four hours the greater part of it had crystallized out. The filtered alcoholic solution was precipitated with water and the semicarbazone thus obtained also recrystallized from alcohol. The combined semicarbazones were then recrystallized once from methyl alcohol with the addition of water, and gave the semicarbazones that were used in determining the melting-points. The results will be found in the table.

Thereupon the α-alkyl-β-naphthocinchoninic acids of O. Doebner[3] were prepared from the three aldehydes in the following manner: 10 grams aldehyde, 6 grams pyroracemic acid, and 10 grams β-naphthylamine were boiled for about three hours in solution in absolute alcohol and the α-alkyl-β-

[1] Ber. d. chem. Ges., **28**, 1957. [2] Ann. Chem. (Liebig), **281**, 19.
[3] Ber. d. chem. Ges., **27**, 2026.

naphthocinchoninic acids recrystallized once from absolutely anhydrous alcohol and used for the determination of the melting-points and for analyses. The results are included in the table already referred to.

The condensation of the three aldehydes with acetone was effected according to the following general method which excludes secondary reactions. Precaution must be taken to avoid these latter as they are apt to take the lead, as is shown by the example which is quoted in the well-known Ionone Patent.[1]

Fifty-gram portions of well dried and freshly distilled aldehyde were dissolved in 50 cc. absolutely dry acetone, and cooled down to 0° at least. Further, 2.5 grams of sodium were dissolved in 50 cc. absolutely anhydrous alcohol, and also cooled down to 0°. Finally, 10 grams tartaric acid were dissolved in 50 cc. water. Then a solution of sodium ethylate was added to the solution of the aldehyde in acetone, the whole being kept cooled and continually stirred, and in fifteen minutes the reaction was interrupted by the addition of the solution of tartaric acid. Now the acetone and alcohol were distilled with water vapor; the residual oil was separated from the solution of tartaric acid and washed. The oil thus obtained after one distillation with superheated steam was rectified either under diminished pressure or purified by means of a solution of sodium bisulphite. For this purpose 50-gram portions of the crude acetone condensation-product were boiled with 100 cc. commercial solution of sodium bisulphite, and 100 cc. water, for about three hours in a vessel connected with an inverted condenser. After the whole was cooled down the small quantities of substances which were not ketones were carefully removed by extracting with ether, and the bisulphite double compound decomposed in the cold with caustic soda. The separated oil was well washed and rectified, first with superheated steam and then under diminished pressure. The analyses and physical constants of the three aldehyde and acetone condensation-products are given in the table farther on.

[1] German patent No. 73089.

The ketones obtained in this way were then characterized by means of their semicarbazones, which were prepared exactly in accordance with the directions given above, with this difference, that they were finally recrystallized, not from methyl alcohol and water, but from a good deal of ligroin boiling at 105°–140°. The melting-points of the semicarbazones are also given in the table.

It is evident from the above table that by means of sodium bisulphite, three aldehydes, $C_{10}H_{16}O$, can be obtained from oil of lemon-grass, which differ distinctly from one another. The condensation-products with acetone also show marked differences, and all can be transformed into different ring-compounds which are ketones having the odor of violets, but none of them gives irone. The geranylidene-acetone gives Tiemann's ionone, while the citriodorylidene-acetone and the allo-lemonylidene-acetone give new ketones with the odor of violet, which form the "artificial oil of violets" of Franz Fritzsche & Co. Besides the naphthocinchoninic acids and the different condensation-products with acetone, the conduct of their compounds with sodium bisulphite is especially characteristic for the three aldehydes themselves.

Citriodoric aldehyde easily forms a very solid compound with bisulphite if not too great an excess of the sodium bisulphite is taken, and the proportion of aldehyde to 35 per cent. sodium bisulphite to water is as 1 : 2 : 2. This solid compound, after standing for a short time, dissolves, forming a clear solution, heat being evolved, and from this the aldehyde can be separated only by means of caustic soda or by boiling with sodium carbonate.

Cinnamic aldehyde, $C_6H_5.CH : CH.CHO$, conducts itself in a similar way. Fr. Heusler[1] has found that it passes into solution in the form of the compound

$$C_6H_5C_2H_3(SO_3Na)CH(OH)(SO_3Na).$$

All aldehydes that contain the group X—CH : CH.CHO seem to have the power to form bisulphite compounds of this kind, and, therefore, considering the relation of citriodoric

[1] Ber. d. chem. Ges., **24**, 1805.

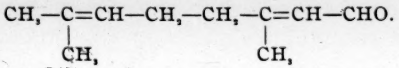
Table Giving the Properties of the Aldehydes ($C_{10}H_{16}O$) *from Oil of Lemon-Grass, and of their Derivatives*

Name / Literature	Citriodoric aldehyde. Dodge: This JOURNAL, **12**, 553.	Citral—Geranial. Tiemann and Semmler: Ber. d. chem. Ges., **26**, 2709; **31**, 820.	Allo-lemonal-Laevo-licarhodal. Barbier: Compt. rend., **122**, 84.
B. p. under 12 mm.	108°–109°	111°–112°	117.5°–119°
B. p. " 760 mm.	228°–229°	225°–227°	233°–235°
Sp. gr. at 20°	0.8883	0.8868	0.9017
Refraction n_D at 20°	1.48538	1.48752	1.48306
Rotation for 1 dm α_D at 20°	± 0°	± 0°	— 5° 5′
M. R. for $C_{10}H_{16}O$ (47.53)	49.07	49.34	48.15
Calc. for $C_{10}H_{16}O$: C = 78.95 p. c.	78.85	79.20	78.77, 79.00
" " " H = 10.53 p. c.	10.95	10.89	11.05, 10.92
M. p. of semicarbazone	134°	141°	169°
α-Semicarbazone }	were not	160° (scales)	could not be
β-Semicarbazone }	separated	150° (needles)	separated
M. p. of naphthocin. acid	204°	197°	235°
Calc. for $C_{21}H_{23}NO_2$: C = 80.00 p. c.	80.00	79.60, 80.20	.....
" " " H = 6.67 p. c.	7.10	7.10, 6.90	.....
" " " N = 4.06 p. c.	4.10	4.10, 4.10	.....
Conduct of the bisulphite compound when heated	Dissolves to a clear liquid, and is separated by NaOH.	Dissolves to a clear liquid, and is not separated by NaOH.	All allo-lemonal separates. It is easily reduced to the alcohol.

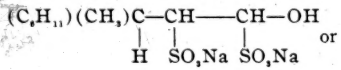
Acetone Condensation-products of the Above Aldehydes.

Name	Citriodoric aldehyde.	Citral—Geranial.	Allo-lemonal-Laevo-licarhodal.
Literature	Dodge: This JOURNAL, **12**, 553.	Tiemann and Semmler: Ber. d. chem. Ges., **26**, 2709; **31**, 820.	Barbier: Compt. rend., **122**, 84.
B. p. under 12 mm.	149°–152°	143°–145°	157°–159°
Sp. gr. at 20°	0.8980	0.9037	0.9000
Refraction n_D at 20°	1.52903	1.52736	1.5315
M. R. for $C_{13}H_{20}O$, 60.94	65.94	65.35	66.05
Calc. for $C_{13}H_{20}O$: C = 81.25 p. c.	81.12	81.17	81.0
" " " H = 10.42 p. c.	10.70	10.77	10.38
M. p. of semicarbazone	134°–135°	110°–112°	142°–143°
Obtained from oil of lemon-grass	40–50 per cent. Citriodoric aldehyde	8–10 per cent. Citral-Geranial	25–30 per cent. Allo-lemonal

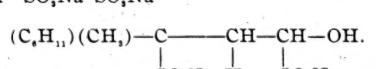
aldehyde to the ketones of the violets (see below), it probably has the following constitutional formula:



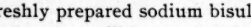
For the easily soluble double compound with bisulphite, the following two formulas are worthy of consideration:

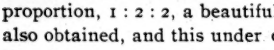


or



Geranial (citral) conducts itself in an entirely different way. This compound is formed in considerable quantity from natural oil of lemon-grass under the influence of strongly acid, freshly prepared sodium bisulphite, as has already been indicated and as will be proved further on; and when geranial (citral) is treated with the same bisulphite in the same proportion, 1 : 2 : 2, a beautiful solid bisulphite compound is also obtained, and this under ordinary circumstances crystallizes in good form after standing for twenty-four hours. If this compound is heated in the liquid in which it is formed, it is partly dissolved and crystallizes out on cooling. If, however, the heating is continued long enough a clear solution is also obtained from which neither sodium carbonate nor caustic soda regenerates an oil either at ordinary temperature or when boiled. According to Tiemann and Semmler,[1] the sodium salt of a true sulphonic acid is formed. In other respects, however, the bisulphite compound of geranial conducts itself perfectly normally, so that it does not contain the end group X—CH : CH.CHO, but must have the formula,



and, therefore, forms the normal bisulphite compound,  , or a salt of the

[1] Ber. d. chem. Ges., **26**, 2710.

sulphonic acid, $(C_6H_9)(CH_3)CH-CH_2-CH\begin{matrix}OH\\SO_3OH\end{matrix}$.

According to its relations to the ionone[1] which has been well investigated, it probably has the following constitutional formula :

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-CHO.$$

Finally, allo-lemonal conducts itself toward sodium bisulphite quite normally, but it differs, nevertheless, essentially from geranial in this respect : Its compound with sodium bisulphite is decomposed at a comparatively low temperature and thus easily regenerates the allo-lemonal. If, therefore, allo-lemonal is shaken with bisulphite and water in the proportion 1 : 2 : 2, a solid bisulphite compound is obtained in a short time, and this when heated yields allo-lemonal again, and does not form a sulphonic acid. While citriodoric aldehyde can be heated repeatedly for any length of time with sodium bisulphite without undergoing a material change, and can be separated afterwards by means of caustic soda ; and while geranial, on the other hand, disappears entirely under these circumstances, allo-lemonal, if heated long enough, is reduced by the hot solution of bisulphite to the corresponding alcohol (allo-lemonol). It appears, therefore, on account of its normal conduct towards sodium bisulphite, that allo-lemonal must also have the formula, $(C_6H_9)(CH_3)CH-CH_2-CHO$.

Further, on account of its optical activity, allo-lemonal must also contain an asymmetric carbon atom. On account of its relations to the ketones of violets, which will be made clear below, it must have the following constitutional formula :

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH=CH-\underset{\underset{CH_3}{|}}{CH}-CH_2-CHO.$$

The existence of three aldehydes, $C_{10}H_{16}O$, in oil of lemongrass is therefore proved with certainty. These are Dodge's

[1] Compare F. Tiemann's formula for ionone, Ber. d. chem. Ges., **31**, 857, 864, 867, 870, 874.

citriodoric aldehyde, the geranial (citral) of Tiemann and Semmler, and Barbier's laevo-licarhodal or allo-lemonal. Certain phenomena which have presented themselves in the course of my investigations, especially the rise of the boiling-point of the mixture of aldehydes above the boiling-point of allo-lemonal, and the existence of a substance which is markedly laevo-rotatory, boiling at a high temperature and having the odor of cedar wood, caused me to suspect that at least a fourth optically active unknown aldehyde of another constitution is contained in oil of lemon-grass; and for this reason I shall continue this investigation in the direction indicated.

III. *Transformations of the Three Aldehydes of Oil of Lemon-grass into One Another.*

If in the preparation of geranial (citral) from the oil of lemon-grass, a large excess of strongly acid freshly prepared sodium bisulphite is used, materially more geranial is obtained than when the commercial solution of the bisulphite is used in the proportion 1 : 2 : 2. If the assumption is made (an assumption which I have shown to be unfounded) that natural oil of lemon-grass contains geranial, and an attempt is made to increase the yield of aldehyde by oxidation of the oil with potassium bichromate and sulphuric acid, it will be found that by means of sodium bisulphite as well as by means of condensation with acetone, much more geranial or pseudo-ionone is obtained than otherwise. From the oil of lemon-grass which is transformed under the circumstances mentioned, the α-geranyl-β-naphthocinchoninic acid melting at 197° is obtained. This is scarcely formed at all under ordinary circumstances.

Barbier and Bouveault[1] first called attention to the fact that the other aldehydes $C_{10}H_{16}O$ are transformed into the most stable one, geranial, by means of acetic or dilute sulphuric acid (or in general by acid agents, even sodium bisulphite). These transformations are similar to those of linalool, licareol, licarhodol into geraniol. I have found, further, that apparently no geranial at all appears to be contained in the oil of lemon-grass, and that this is formed by the transformation of

[1] Compt. rend., 122, 84–86.

the citriodoric aldehyde and allo-lemonal, as pure oil of lemon-grass which has not been brought in contact with acids gives no pseudoionone nor ionone, as I have often shown experimentally.

If, however, the oil of lemon-grass is previously treated with sulphuric acid, abundant quantities of pseudoionone and ionone are obtained in consequence of condensation or rearrangement.

It follows from this that only geranial (citral) or oil of lemon-grass that has been completely transformed by means of sulphuric acid, bisulphite, etc., can yield pseudoionone and ionone, while natural oil of lemon-grass can give only citriodorylidene and allo-lemonylidene-acetone whose cyclic ketones form the "artificial oil of violets" of Franz Fritzsche & Company. But I have observed also another kind of transformation of the three aldehydes: If perfectly pure geranial[1] is boiled with a 20 per cent. solution of sodium acetate for some hours, an oil is obtained that boils at 108°–119°, and the lowest fraction of this oil conducts itself like citriodoric aldehyde. The middle fraction is unchanged geranial, and the highest one conducts itself like allo-lemonal towards sodium bisulphite, as well as in regard to the melting-point of its naphthocinchoninic acid. The sodium acetate under these circumstances seems to act as a very weak alkaline reagent, and it appears that under certain conditions more strongly alkaline agents and the carbonates of the alkalies first effect a similar transformation before they act further upon the aldehydes.

In natural oil of lemon-grass, therefore, only citriodoric aldehyde and allo-lemonal are contained, because in the condensation with acetone with the aid of sodium alcoholate, only citriodorylidene- and allo-lemonylidene-acetone are obtained, and because, according to this method, as is also noted by F. Tiemann, "other chemical changes need not be feared," as this condensation takes place at very low temperature, in a

[1] Boiling at 111–112° under 12 mm. pressure forming a naphthocinchoninic acid melting at 197°, and conducting itself towards bisulphite in a manner characteristic of geranial.

very short time, with very little alkali, in a solution absolutely free from water.

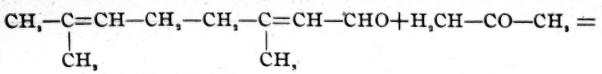
By the action of acid reagents upon oil of lemon-grass more or less abundant quantities of geranial are formed which give more or less pure pseudoionone when condensed with acetone.

By treating with weak alkaline reagents, acid salts of organic acids, etc., geranial can be transformed into citriodoric aldehyde and allo-lemonal.

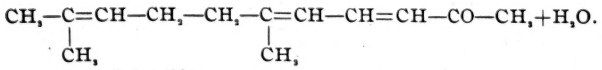
IV. *Relations of the Three Aldehydes of the Oil of Lemon-Grass to the Ketones of the Violet.*

In one of the preceding paragraphs I have suggested constitutional formulas for the three aldehydes, taking into consideration the somewhat complicated literature, and the conduct of these substances as observed by me. As all three of the acetone condensation-products form violet ketones by closing the ring, I place the formulas all together.

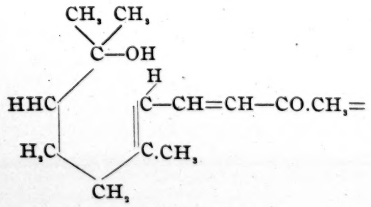
A. *Citriodoric Aldehyde.*



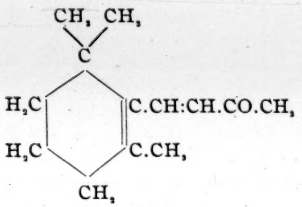
Citriodoric Aldehyde. Acetone.



Citriodorylidene-acetone.

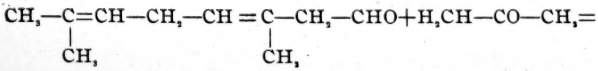


Hydro-citriodorylidene-acetone.

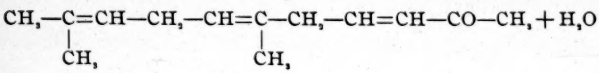


Cyclo-citriodorylidene-acetone.

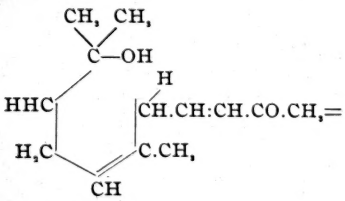
B. *Geranial (Citral).*



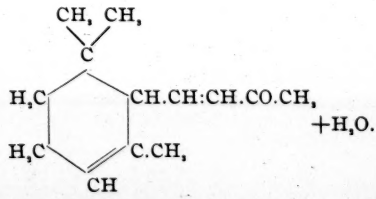
Geranial (citral). Acetone.



Geranylidene-acetone.

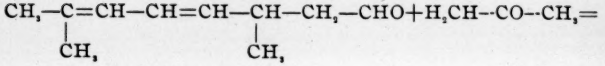


Hydro-geranylidene-acetone.

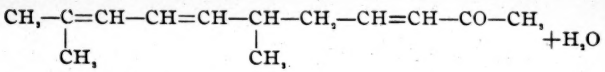


Gyclo-geranylidene-acetone.

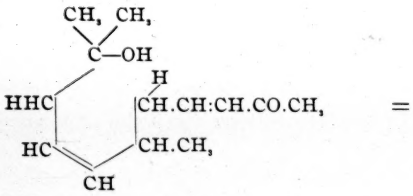
C. *Allo-lemonal (Laevo-licarhodal).*



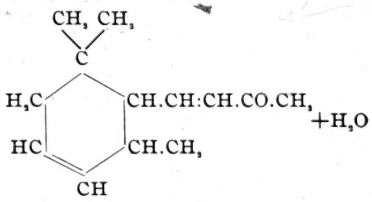
Allo-lemonal (Laevo-licarhodal). Acetone.



Allo-lemonylidene-acetone.



Hydro-allo-lemonylidene-acetone.



Cyclo-allo-lemonylidene-acetone.

Upon the basis of his extensive investigations of irone and ionone,[1] F. Tiemann reaches the conclusion that the existence of four structurally isomeric substances can be foreseen, and that all of these may be expected to have the odor of violets. Three of these four formulas of violet ketones are identical with those which I have presented above.

The cyclo-citriodorylidene-acetone is identical with Tiemann's second hypothetical violet ketone.

[1] Ber. d. chem. Ges., 31, 867.

The cyclo-geranylidene-acetone is Tiemann's ionone.

The cyclo-allo-lemonylidene is Tiemann's first hypothetical violet ketone.

The fourth violet ketone is natural irone, the synthesis of which has not thus far been effected.

I intend later to publish a more complete investigation of these violet ketones, the formation of which, from the three aldehydes described by me, takes place very simply, and thus furnishes the confirmation of F. Tiemann's theory of the existence of four violet ketones of definite constitution.

The present investigation further places in a clear light the very complicated relations presented in the last publications of F. Tiemann, and his coworkers on the subject of ionone. In his first classical treatise on the aroma of violets,[1] as well as in his patents,[2] and also in the communication on methods of detecting ionone and irone,[3] Tiemann has given the properties of ionone and pseudoionone and their reactions with great accuracy, and he has also stated that these substances were prepared from pure materials (geranial-acetone),[4] and had been obtained in chemically pure condition.

As F. Tiemann[5] in one of his last publications says that citral (geranial) is, up to the present, the only aliphatic terpene aldehyde of the formula $C_{10}H_{16}O$, the presence of which has been established in ethereal oils, and thus shows that he does not recognize the existence of citriodoric aldehyde and allo-lemonal, it appears that he has of late used fractionated oil of lemon-grass for the preparation of his ionone, and I have already shown that this consists principally of citriodoric aldehyde and some allo-lemonal, for only in this way is it possible to explain why the pseudoionone and ionone which at first were so sharply characterized, have become so changeable in their constants and reactions.[6]

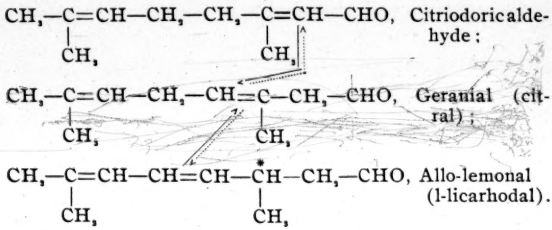
With the aid of this assumption, it is also possible to see why he now obtains from the ionone a whole series of different

[1] Ber. d. chem. Ges., **26**, 2692.
[2] German Patent No. 73089.
[3] Ber. d. chem. Ges., **28**, 1754.
[4] *Ibid.*, **26**, 2692.
[5] *Ibid.*, **31**, 822.
[6] Compare *Ibid.*, **26**, 2692, with *Ibid.*, **31**, 842, 851, 879.

semicarbazones, for ionone[1] is nothing but the cyclo-allo-lemonylidene-acetone described above, while besides the true ionone the cyclo-citriodrylidene-acetone must also be contained in these products.

It follows from this that Tiemann's ionone can be prepared only from pure geranial, or from sufficiently transformed oil of lemon-grass (citral), while the natural oil of lemon-grass, as well as the separate aldehydes, citriodoric aldehyde and allo-lemonal, must always give the ketones of the "artificial oil of violets" of Messrs. Franz Fritzsche & Co.

In conclusion I give the three constitutional formulas for the aldehydes as they have been deduced from their chemical conduct and from their relations to the violet ketones, and at the same time their transformations are indicated:



The arrows show the passage from citriodoric aldehyde and allo-lemonal to geranial under the influence of acid reagents. The arrows drawn in broken lines show the passage from geranial to citriodoric aldehyde and allo-lemonal under the influence of alkaline reagents. The star indicates the asymmetric carbon atom in allo-lemonal.

In these transformations there occurs only a change of position of one double bond in the aldehydes, either to or from the position of equilibrium in geranial.

This memoir will appear in full in the "Journal für praktische Chemie."[2]

HAMBURG, Aug. 1, 1898.

[1] Ber. d. chem. Ges., **31**, 867–881.

[2] See J. prakt. Chem., N. F **58**, 51.

THE FREEZING-POINT, BOILING-POINT, AND CONDUCTIVITY METHODS. By HARRY C. JONES, Instructor in Physical Chemistry in Johns Hopkins University. Easton, Pa.: The Chemical Publishing Co. 1897. 64 pp. 75 cents.

This little book is a laboratory guide and presents the necessary details for making determinations of molecular weights by the new methods, and for studying the conductivity of solutions, while, at the same time, the theory of the subject is not forgotten. It will no doubt be found useful wherever the methods it treats of are taught—that is to say, in all chemical laboratories where physical chemistry is recognized as an important and necessary part of chemistry.

In describing the boiling-point method, the author confines himself largely to a form of apparatus devised by himself, upon the basis of one previouslv described by Hite. This gives his work a somewhat one-sided air, but, after all, it was not his purpose to describe all methods in detail, but rather to lay stress upon what appeared to him the simplest and best. His apparatus is simpler and cheaper than that of Beckmann, and, to say the least, gives as good results. Apparently it gives better results.

COMMERCIAL ORGANIC ANALYSIS. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicine, with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By ALFRED H. ALLEN, F.I.C., F.C.S. Past President Society of Public Analysts, Public Analyst for the West Riding of Yorkshire and the City of Sheffield, and the Boroughs of Chesterfield, Doncaster, Rotenham, etc. Third Edition, Illustrated with Revisions and Addenda by the Author, and by HENRY LEFFMANN, M.A., M.D., Professor of Chemistry and Metallurgy in the Pennsylvania College of Dental Surgery, and in the Wagner Free Institute of Science, Philadelphia, etc.—VOLUME I.—*Introduction, Alcohols, Neutral Alcoholic Derivatives, Sugars, Starch and its Isomers, Vegetable Acids, etc.* Philadelphia: P. Blakiston's Son & Co. 1898. 557 pp. Price $4.50.

Allen's "Organic Analysis" consists of four volumes. Two editions of each of the first three volumes have been published, and now, simultaneously, the third edition of Volume I, and the second edition of Volume IV are brought out. A notice of the latter will appear in this Journal later. The author has had all he could attend to in preparing the second edition of his book, which is only just finished. Meanwhile the second edition of the earlier volumes has been exhausted, and

some of the volumes are out of print. Taking advantage of the fact just mentioned a publisher has reprinted Volume I, without consulting the Author. In order now that the publisher may be punished, as he certainly deserves to be, the Author has secured the cooperation of Dr. Henry Leffmann, in the preparation of the needed third edition. A copy of an affidavit is sent out with Volume I, from which the following passage is taken: "The earlier volumes of the above work being out of print he (the author) has authorized Messrs. P. Blakiston's Son & Co. to reprint these earlier volumes with such additions and corrections as they may think proper." He further says "that to facilitate this he has supplied Dr. Henry Leffmann, of Philadelphia, with numerous and valuable addenda with full discretion to use these as he may think fit; that the work as thus revised is the only issue authorized by him in any way in the United States of America, that he has carefully examined the reprint of Volume I of 'Commercial Organic Analysis' recently issued, and finds that it misrepresents his present views in regard to a large number of matters, even the errata which were discovered after the publication of Volume I, and lists of which were published in the later volumes, remaining uncorrected in this reprint; that he protests strongly against the issue of this unauthorized and uncorrected reprint of a book fourteen years old, which issue has been effected without his knowledge or concurrence, and that Messrs. P. Blakiston's Son & Co. are his authorized agents and publishers in the United States of America."

The facts stated in this affidavit should be known to every chemist, but especially to those who have bought or are intending to buy the book.

Allen's "Organic Analysis" is so well known that it is unnecessary to review the new volume in detail. Those who are engaged in analytical work cannot do without it. It is such a book as can be written only by a chemist who has had extensive experience in dealing with practical chemical problems, and one who is also a careful student and investigator.

This volume, as the title-page informs us, deals with "alcohols, neutral alcoholic derivatives, sugars, starch and its isomers, vegetable acids, etc." "The neutral alcoholic derivatives" treated of are ether, compound ethers (esters), aldehydes, chloral, chloroform. Under "alcohols" methods for the analysis of wine, cider, malt liquors, spirits, liqueurs or cordials, and tinctures are given. There are many inter-

esting revelations regarding adulterations. Thus, on page 161 occurs this statement: "The green color of absinthe ought to be due to chlorophyll, introduced from spinach nettles, or parsley. A mixture of sulphate of indigo with picric acid or turmeric is not unfrequently employed, and salts of copper have also been used." Among the substances liable to be found in bread are "magnesium carbonate, alum and equivalent preparations containing aluminium, plaster of Paris, whiting, and barium sulphate (page 449). On page 453 it is stated that "*Sulphate of Copper* was formerly employed as an adulterant of bread, especially in foreign countries, and a recent instance of its employment in this country has been recorded." In regard to honey we are told (page 381) that it "is frequently adulterated, the most common sophistication being the addition of glucose syrup, a dextrinosaccharine liquid obtained by the action of dilute acid on starch. A factitious honey is sometimes manufactured wholly from glucose syrup, with addition of minute quantities of formic acid, and flavors to give the preparation the flavor of honey."

While these and many other similar statements are interesting reading, it must be said that, for the most part, the adulterating substances are used in such minute quantities as to be of no importance from the sanitary point of view.

A few slips have been noted. On page 37, Frauenhofer is spelled "Frauenhöfer"; and on page 257 "Schiebler" occurs instead of Scheibler. Under chloroform (page 232), the author states that this substance is prepared from alcohol and from chloralhydrate. In a foot-note he says; "Acetone * * may be substituted for alcohol in the preparation of chloroform." The reader would get the impression that acetone is used, if used at all, only to a slight extent; whereas, as a matter of fact, in Germany and in this country at least, very large quantities of chloroform are manufactured from acetone.

According to the classification now adopted by chemists the polyatomic alcohols, such as mannite and dulcite, are not called sugars. The author says (page 243): "Glycerol and glycol have a sweet taste, and, like the sugars, are polyatomic alcohols;" and, also: "Most of the sugars have the constitution of hexatomic alcohols, or of aldehydes or ethers derived therefrom. True mannite, which is α-hexone alcohol, $C_6H_8(OH)_6$, by limited oxidation with platinum-black yields the corresponding aldehyde, $C_6H_8(OH)_5$, which is a true sugar called mannitose." Of course, the formula given for mannitose is wrong. It should be, $C_6H_8(OH)_5CHO$. The "American Academy of Sciences," referred to on page 369, should be "The National Academy of Sciences."

Most of the slips noticed are, however, of little importance. The book is excellent, as all chemists know, and it will continue to be the standard in the subject with which it deals. I. R.

A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS. By E. F. LADD, B.S., Professor of Chemistry in the North Dakota Agricultural College, and Chemist to the Government Experiment Station, Fargo, N. D. New York: John Wiley & Sons. 82 pp. 1898.

The author has prepared this book for beginners, and has selected methods which he says are not always the ones which will give the most reliable results, but are such as will aid in developing the reasoning powers of the student. The explanation of details has been omitted as the student is expected to refer to larger works for these facts. The book contains, besides general directions, methods for gravimetric and volumetric analyses of metals, acids, etc., and methods used in the analysis of ashes, soils, ores, food-stuffs, water, and urine. The student could not get a clear idea of the chemical principles involved from the very condensed form of the directions as given here, and it would perhaps be more satisfactory if the part relating to such subjects as water and urine analyses was omitted, and the general principles explained more fully, as such works as those of Fresenius and Crookes are not always available and are themselves very mechanical. These difficulties can, however, be overcome by a competent instructor, and under such a director the book would perhaps prove as successful as it has in the hands of the author. J. E. G.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS. By HENRY W. SCHIMPF, Professor of Inorganic Chemistry in the Brooklyn College of Pharmacy. Third Edition. New York: John Wiley & Sons. 1898. pp. xxix, 522.

It is one of the unfortunate evils of our educational system that a text-book should have to be written for a particular class of students instead of dealing with a subject in a manner broad enough to be suitable for all classes. In his preface the author, states that the book "is designed for the use of pharmacists, and especially as a text-book for students in pharmacy." This is more or less of an admission that there is either something wrong with the subject, or with the students, and we are inclined to believe that it is the poor preliminary training of the students. The pharmacist—and the book will be useful only to pharmacists—after he has done most of the experiments will not have obtained a clear, general idea of volumetric analysis, but will have received a

certain mechanical training in the determination of certain substances. The U. S. Pharmacopoeia has been taken as the basis of the book, and this is mostly responsible for the manner of treating the subject. The author has accepted the conditions as they have existed for a number of years without trying to improve upon the method of presenting the subject.

The book is divided into four parts treating of: I. "A Systematic Arrangement of Volumetric Processes" including pharmaceutical methods for inorganic substances. II. The Volumetric Analysis of Various Medicinal Acids and Salts. III. Sanitary Analysis. IV. Gasometric Analysis.

The first part treats of general principles, apparatus, standard and normal solutions, indicators, and calculations and then proceeds to the preparation of standard solutions. For each solution prepared the author gives the reaction taking place, neutralization or precipitation as the case may be, and directly under the equation gives the molecular weight of each substance and shows the number of grams to the litre for the reactive reagent; thus on pages 64–68, the reaction of sulphuric acid with eight separate carbonates is written out, and as many times the student is shown that there are 49 grams of H_2SO_4 entering the reaction. On pages 115–128 we see at least sixteen times the reaction of silver nitrate on chlorides, iodides and bromides, with molecular weights and almost as many examples of calculations. This endless repetition of reactions, with their corresponding figures, is not confined to any one class of reactions but is general throughout the book. There are extremely few generalizations, the subject matter is not logically developed, and there is no attempt made to show the reliability or accuracy of the various methods. Much space is consumed by repetitions of a process for different salts of the same acid as in the case of hypophosphorous acid on pages 163–169, where the reactions and process are repeated for the calcium, iron, potassium and sodium salts, when one statement of the reaction of all would have been sufficient.

Part III, treating of the sanitary analysis of water, milk, butter, soap, wine, and analysis of drugs and alkaloids is free from most of the objections raised against the rest of the book.

The illustrations, with few exceptions, show forms of apparatus which for the most part are never used, such as the various obsolete forms of burettes. H. F.

A Manual of Chemical Analysis, Qualitative and Quantitative. By G. S. Newth, F.I.C., F.C.S. New York & London: Longmans, Green & Co. 1898.

In this book of 462 closely printed pages, the first 186 pages

are given to qualitative analysis, 106 to gravimetric, 114 to volumetric methods, and 30 to analysis of organic compounds and physical chemical determinations. An appendix contains useful tables. The book is good, and sufficiently thorough for college and technical students. It is well illustrated with plates of apparatus and manipulation. It is scarcely necessary to say to those familiar with the author's excellent book on "Lecture-room Experiments" that the methods are good and that they are clearly described. Prof. Newth's book is recommended to those who desire a book covering the entire field. E. R.

AN INTRODUCTION TO THE SCIENCE AND PRACTICE OF QUALITATIVE CHEMICAL ANALYSIS, INORGANIC. By CHAPMAN JONES, F.I.C., F.C.S. London & New York: Macmillan & Co. 213 pp. $1.50.

Still another manual of analysis combining to some extent a text-book of chemistry with an analytical manual by including part, but not all of the average text-book information. The book is clearly written has the 'table' system in pronounced degree, is as good as most other manuals of the same type but offers nothing new. E. R.

CHEMICAL AND METALLURGICAL HANDBOOK, containing Tables, Formulas, and Information for the use of Chemists, Metallurgists, and Mining Engineers. By J. H. CREMER, M.E., and G. A. BICKNELL, M.S. Second Edition. Cleveland, Ohio. 1898.

This little book is something on the order of the German Chemiker-Kalender, though it does not contain as much. The Table of Molecular Weights, Specific Gravities, Melting-points, Boiling-points, and Solubilities of the Principal Inorganic Compounds (pages 24–54) is highly suggestive of Biedermann's book. There are tables of all sorts presented. Among them the following may be specially mentioned: Analytical reactions, specific gravity of alcohol, sulphuric acid, hydrochloric acid, nitric acid, of ammonia and the caustic alkalies, methods for analysis of iron ore, pig iron, steel, coal and coke, minerals, methods used in assaying, logarithms, etc., etc. The book appears to be worthy of commendation.

Correction.

Vol. 19, page 404, line 15: *For* "114°" *read* "119°–120°."